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# SOIL SCIENCE

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## CALCIUM SYMPOSIUM

This issue of SOIL SCIENCE is made up of a series of papers on calcium, which were presented before the Division of Fertilizer Chemistry of the American Chemical Society at its annual fall meeting held in the Pennsylvania Hotel in New York City on Tuesday, September 16, 1947. The meeting was attended by some 200 chemists who were interested in knowing more about calcium as an essential element in the growth and development of green plants and of animals and man. The papers are intended to present a fairly complete picture of our present knowledge of this element as a nutrient, as a soil constituent, and as an ingredient of fertilizers. We are pleased to be able to publish them for the benefit of the readers of this Journal.

FIRMAN E. BEAR.

## LIME IN RELATION TO AVAILABILITY OF PLANT NUTRIENTS

EMIL TRUOG

*University of Wisconsin*

In agricultural terminology, the word *lime* refers to the carbonate, hydroxide, and oxide of calcium and, to a lesser degree, of magnesium. Lime is added to soils to neutralize acidity, supply calcium and magnesium as nutrients for plant growth; and improve the physical condition of soils by providing a high level of exchangeable divalent cations which tend to coagulate the colloids. This paper deals primarily with the first purpose, because it is largely through the effect on soil reaction that lime influences availability of plant nutrients.

An extensive literature shows that availability of all nutrient elements obtained by plants from the soil is influenced to some degree by the level of lime present. When the levels of exchangeable and carbonate forms of calcium and magnesium are too high, availability is in some cases adversely affected. The reasons for both the favorable and the unfavorable influence of lime on this availability have been greatly clarified in recent years. A discussion of these matters is presented here, along with a chart which illustrates the general trend of the relation of reaction and accompanying conditions to the availability of plant nutrient elements.

In 1935, Pettinger<sup>1</sup> of the Virginia Station published a very useful chart showing the relation of soil reaction to the availability of seven plant nutrients. The chart presented here (fig. 1) shows this relation in connection with eleven nutrient elements, and is simpler in form but more complete in several respects than the Pettinger chart.

### *Explanation of Chart*

In this chart, reaction is expressed in terms of the pH scale. The change in intensity of acidity and alkalinity from one pH value to another is shown graphically in the diagram by the change in width of the heavily cross-hatched area between the curved lines.

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<sup>1</sup> Pettinger, N. A. Useful chart for teaching the relation of soil reaction to the availability of plant nutrients to crops. *Va. Agr. Ext. Bul.* 136: 1-19, 1935.

The influence of reaction on availability of each nutrient element is expressed by the width of the band (the wider the band, the more favorable the influence) carrying the name of the respective element. Thus, for the maintenance of a satisfactory supply of available nitrogen, for example, a reaction or pH range of 6 to 8 is the most favorable. This does not mean that if the reaction of a soil falls in this range a satisfactory supply of available nitrogen is assured. All it means is that so far as reaction is concerned, the conditions are favorable for a satisfactory supply of this element in available form. Also, the narrowed band for nitrogen at pH 5 does not necessarily mean that a deficiency of this element will

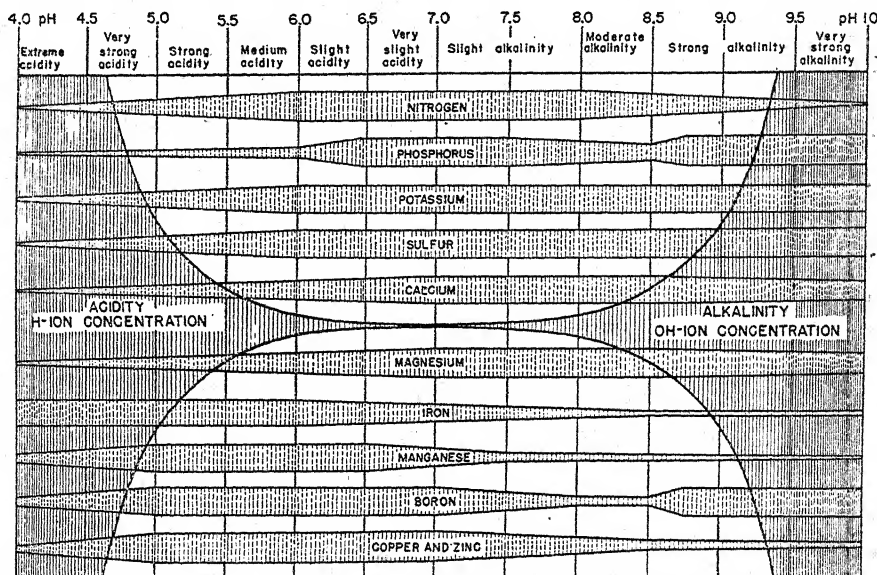


FIG. 1. CHART SHOWING GENERAL TREND OF RELATION OF REACTION TO AVAILABILITY OF PLANT NUTRIENTS

Width of bands indicates *favorableness of reaction influence* to the presence of adequate amounts of the nutrients in readily available forms, and not to actual amounts necessarily present; these amounts are influenced by many other factors.

prevail at that pH; it means that so far as reaction is concerned, the conditions are not favorable for an *abundant* supply in available form. Other factors than reaction may promote the presence of an abundant supply; moreover, certain crops having a low requirement may be fully satisfied with a low supply.

#### NITROGEN

At both strong acidity and strong alkalinity, the conditions for nitrogen fixation by legumes and transformation of organic nitrogen to forms available to plants become increasingly less favorable. Since alfalfa is one of the best plants for fixation of atmospheric nitrogen, but usually does not do this satisfactorily unless the pH is at least 6.5, the great importance of an adequate supply of lime in this connection is fully apparent. Although some legumes grow and fix nitrogen satisfactorily at a much lower pH than 6.5, they nevertheless draw heavily on the calcium supplies of the soil, making necessary frequent additions of lime.

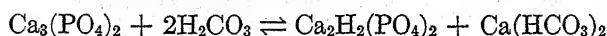
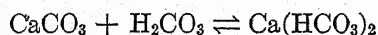
Ammonification is not retarded by soil acidity until this acidity becomes strong. This is due to the neutralizing effect of the ammonia produced, and also to the marked tolerance of ammonia-producing organisms (fungi, to a large extent) for acidity. The oxidation of ammonia to nitrous acid by nitrosomonas and other related species, and of nitrite to nitric acid by nitrobacter is markedly retarded, however, by soil acidity. This is due to the sensitivity of these organisms to the acidity which develops when the nitrous and nitric acids are not neutralized, as is the case naturally in an acid soil. That is why the application of lime to distinctly acid soils often greatly stimulates nitrification and thus the production of readily available nitrogen. The most favorable reaction range for nitrification lies in the pH range of 6 to 8. In this range the nitrous and nitric acids as formed are, for the most part, soon neutralized by either exchangeable or carbonate calcium.

#### PHOSPHORUS

Figure 1 shows that between 6.5 and 7.5 conditions are most favorable for phosphate availability. Below pH 6.5, the influence on availability rapidly becomes less favorable. That is an important reason why, for general farming, acid soils should usually be limed to pH 6.5. In fact, if lime produced no other benefit than its favorable influence on phosphate availability, it would usually pay to use it. At pH 6.5, calcium bicarbonate becomes sufficiently abundant in the soil solution to keep a considerable portion of the phosphorus in the form of calcium phosphate, which is soluble in carbonic acid and, hence, readily available to crops. This holds for both the phosphorus naturally present in soils and that applied in the form of manures and fertilizers.

As the pH drops to 6.0 and less, a marked drop in the availability of calcium and in the concentration of calcium bicarbonate in the soil solution occurs. Accordingly, the tendency to form calcium phosphate decreases, and increasing amounts of basic ferric phosphate are formed by combination with hydrated iron oxides; in this form the phosphate has a much lower availability. Also, with a drop in pH, small amounts of iron dissolve and appear in the soil solution. This iron may also react to form ferric phosphate. Combination of the phosphate with aluminum oxides and silicates also tends to increase as the pH drops. In all of these forms, the phosphorus has a lower availability than in tricalcium phosphate, except possibly when calcareous soils are involved. Since hydrated iron oxides are usually abundant in soils, and phosphate when combined with these has a very low solubility, the tendency for this combination in most soils is much greater than the tendency for a combination with silicates.

When lime is present or is added in amounts so as to raise the pH beyond 7.5, the influence on phosphate availability gradually becomes less favorable, although this is usually not serious until the pH goes beyond 8 and there is present 2 to more than 3 per cent of free calcium carbonate. The reason for this is shown by the following reactions:





The solubility of all of the products formed is low but adequate for plant nutrition. It will be noted that calcium bicarbonate is formed in both reactions. Now, if a great abundance of calcium carbonate is present in a soil, action of carbonic acid on it will keep the soil solution saturated with calcium bicarbonate, and this will greatly retard or even stop the second reaction because it also involves the formation in solution of calcium bicarbonate. In other words, when the soil solution is once saturated with a certain product such as calcium bicarbonate, all reactions involving the formation of this product are brought to a stand still until some of the product is removed by leaching or plant feeding. This explanation accords with the well-known law of mass action. Observations indicate that usually a soil must contain several per cent of calcium carbonate, that is, enough to surfeit all the minute areas, in order seriously to retard phosphate availability. Of course, since 1 per cent of calcium carbonate in a soil represents 10 tons of lime per acre, a condition of this kind is seldom, if ever, produced by liming.

As the pH goes up to 8.5 and higher, a tendency should develop for the formation of sodium phosphate, which, being soluble, would be readily available for plant use. Experience with soils having a pH of 8.5 or higher is that they are usually well supplied with available phosphorus.

#### SULFUR

The chart shows that conditions associated with acidity, especially of a pronounced degree, are unfavorable to availability of sulfur. At strong acidity, the conditions for both the accumulation of sulfur in organic matter and its subsequent transformation to sulfate for plant use are not especially favorable. Sulfates, unlike phosphates, are not fixed chemically in difficultly available forms, regardless of the pH; consequently as regards availability and mobility, sulfur is more nearly like nitrogen than phosphorus. Sulfates serve as an ideal source of readily available sulfur for plant use; they are, however, subject to leaching, and as a result, considerable amounts of sulfur are lost annually in this way under conditions that are favorable for the production of strong acidity. Since smoke from coal contains large amounts of sulfur in the form of oxides, however, the atmosphere in heavy coal-burning areas contains considerable sulfur which is brought down in rain and snow; the amount thus added ranges from 10 to 50 pounds per acre annually and compensates largely or entirely for losses by cropping and leaching. The sulfur derived from the atmosphere is largely in the form of sulfate. Appreciable amounts are also absorbed directly from the air by moist soil and snow cover.

At a pH of 6 and higher, conditions as regards reaction are uniformly favorable for the presence of adequate amounts of sulfur in available form. Since high pH is usually associated with restricted leaching, it also is usually associated with an abundance of sulfates, which accumulate because of little loss by leaching.

The fact that sulfur is not fixed in difficultly available form in the soil, is added as an incidental constituent of fertilizers, such as superphosphate, and is brought down by rain and snow, makes it rather easy to maintain an adequate supply of

readily available sulfur in soils. Special sulfur fertilization is necessary, however, in a few areas, particularly in the states of Oregon and Washington, where additions by means of rain and snow are meager because of the purity of the air blown in from the Pacific Ocean.

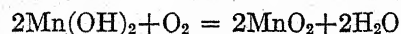
#### POTASSIUM, CALCIUM, AND MAGNESIUM

With increasing acidity, the amounts of potassium, calcium, and magnesium that exist in exchangeable or readily available form usually decrease, and these elements are also held more tightly by the excess of exchange acids against solution and plant feeding. There is little or no evidence that a pH above 7 is seriously unfavorable to the availability of these three elements, although calcium and magnesium probably become somewhat less soluble above pH 8.5 because of the presence of sodium carbonate. The addition of lime provides calcium, and in the case of dolomitic lime also magnesium, in available form. There is some evidence that in certain soils the addition of lime promotes the transformation of fixed potassium to a more available form.

#### MANGANESE

The influence of reaction on availability of manganese is very marked. Although it has been known for 20 or more years that high pH or heavy liming sometimes induces a deficiency of available manganese, it was not until recent years that the frequency of this occurrence became established by means of controlled experiments. The amount of manganese required by plants is low, a ton of alfalfa hay usually containing about 1 pound.

The supply of available manganese in sands and loams low in organic matter and in certain peats low in manganese-containing minerals is frequently too small for crop needs when the pH rises above 7, and especially when the soils are calcareous. The explanation for this is now quite clear. As long as the soil is acid, a considerable portion of the manganese tends to exist in the divalent form. In this form it reacts like calcium or magnesium, particularly as an exchangeable cation and in its ready availability, because it is brought into solution as a bicarbonate through the action of the ever-present carbonic acid. As the pH rises to 7 and higher, the tendency for the oxidation of divalent manganese to the tetravalent form by the oxygen dissolved in the soil solution greatly increases. This proceeds in accordance with the following reaction:



Tetravalent manganese in the form of manganese dioxide is insoluble in carbonic acid and is, therefore, not readily available for crop use.

Since oxygen is required in the above reaction for the formation of the highly insoluble manganese dioxide, excessive aeration of the soil also favors this formation. Thus, a combination of high pH and excessive aeration is the condition under which a lack of available manganese most frequently occurs. Because sands and loams which are low in organic matter and water-holding capacity are often overaerated, it is these kinds of soils that are most subject to a lack of available

manganese when the pH is high. Some peaty and sandy soils are so low in total manganese that even when strongly acid they lack an adequate supply of this element in available form. At strong acidity, a low supply of total manganese may become depleted rather rapidly by leaching.

On the other hand, the heavier soils, and those containing considerable organic matter, hold much more water and do not easily become overaerated; in fact, a lack of aeration often occurs in the heavier soils, especially during periods of heavy rainfall. These soils are usually also better supplied with organic matter, which on decomposition releases its manganese in available form and favors transformation of manganese minerals to the available type. Thus a lack of available manganese at high pH occurs much less frequently in the heavier soils than in the lighter ones.

#### IRON

Reaction influences availability of iron in much the same way as it does that of manganese, but because of the great abundance of iron in soils compared to manganese, deficiency of available iron is not nearly so common as deficiency of available manganese. Below pH 6.5, small amounts of iron tend to exist in the ferrous state; in this form the iron is soluble in carbonic acid and, hence, is readily available. In fact, at extreme acidity and restricted aeration, toxic concentrations of ferrous iron sometimes exist. Also, at strong acidity, the ferric oxide, which is always present, dissolves in sufficient amounts to supply crop needs. As the pH rises above 6.5, soluble ferrous iron tends to become oxidized to ferric oxide, which is so insoluble under neutral and alkaline conditions that a deficiency for crop growth sometimes occurs. As is the case with manganese, a good supply of active organic matter tends to overcome a lack of available iron at high pH because it not only carries and furnishes available iron, but also produces local reducing areas where iron is kept in the readily available ferrous state.

#### BORON

In this country, Naftel<sup>2</sup> of Alabama was the first to demonstrate the relation of overliming or high pH to a deficiency of available boron. Boron is required in small amounts (a ton of alfalfa hay may contain about an ounce) by all crops for normal growth. The amount present in fertile soils in available form, that is, extractable with hot water, is usually not more than 1 to 5 pounds per acre plow-layer. In some soils, particularly those that are low in organic matter and have been severely leached and exhaustively cropped, as is the case with many sandy soils of the South and Southeast, the content of available boron is so low that a slight reduction in availability, such as may be effected by liming, to a pH above 7, greatly reduces crop yields. The application of 25 to 50 pounds of borax per acre completely remedies the condition; in consequence, the lime needed to raise the pH so as to grow alfalfa, clover, and other crops successfully may be added.

<sup>2</sup> Naftel, James A. *Jour. Amer. Soc. Agron.* 29: 761-771, 1937.



At very high pH, that is, 8.5 and higher, the influence of reaction on availability of boron should be similar to the influence on availability of phosphorus. At any rate, an inadequate supply of available boron seldom, if ever, occurs in this high pH range. In fact, toxic concentrations frequently develop because of little or no removal by leaching.

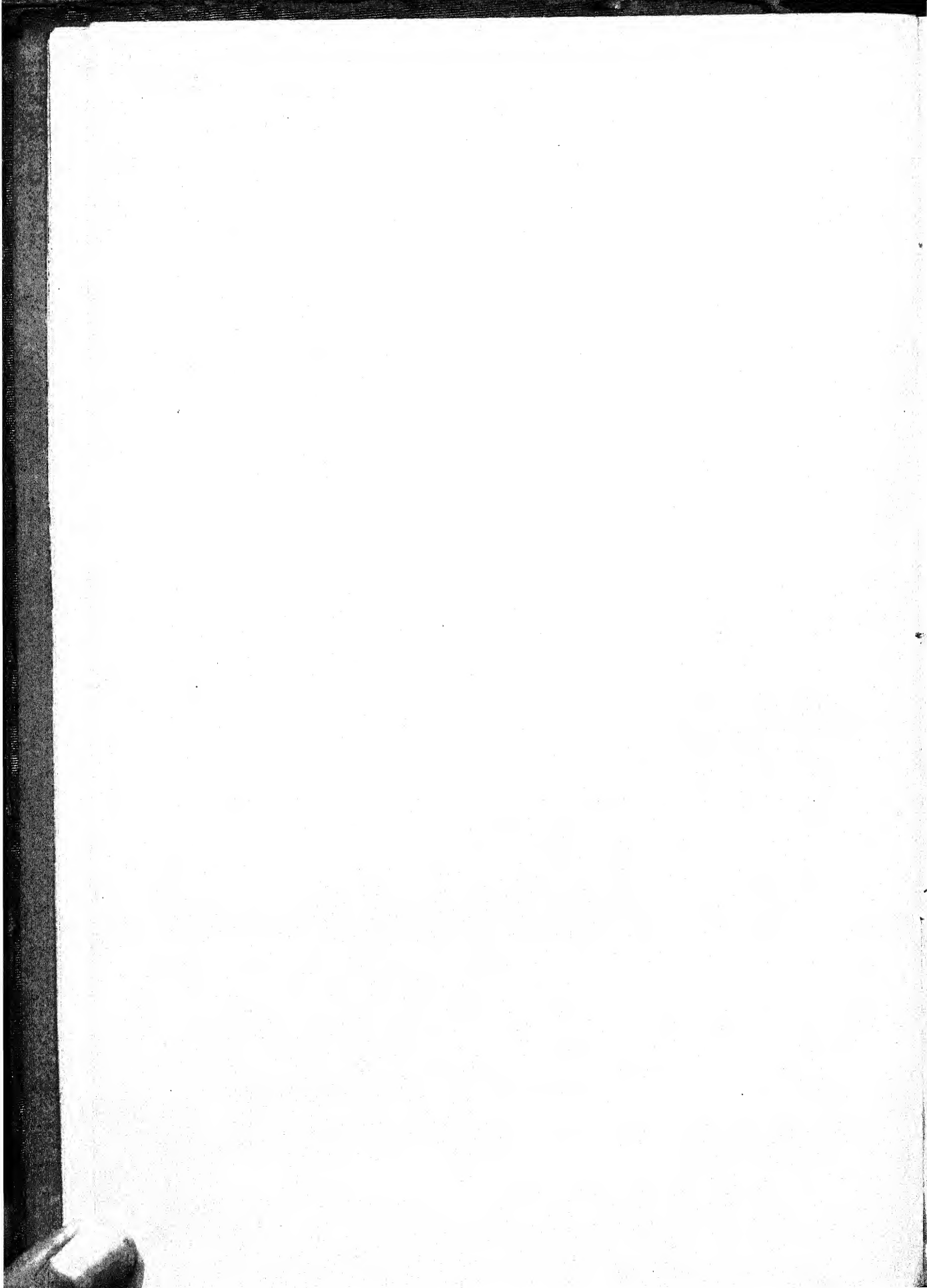
#### COPPER AND ZINC

Copper and zinc are required by crops in only minute amounts. Because the content of these elements in soils is usually very low, however, deficiencies sometimes occur, particularly under calcareous and highly alkaline conditions, which greatly lower solubility and availability of these nutrients. Also, in strongly acid soils, the amount of these elements present in readily available forms may be too low for crop needs because of depletion by leaching during the development of the acidity and because of strong retention by the soil acids of the remaining portions which exist as exchangeable bases.

#### CHART IS GENERALIZED

It must be emphasized that the chart is a generalized presentation. Because adequate and precise data relating to certain aspects of this subject are still lacking, some assumptions had to be made in the preparation of the chart, and this has undoubtedly led to certain inaccuracies. Cases which do not conform to the chart as drawn will occur because of these inaccuracies or because of special and peculiar conditions that happen to be involved. In the main, however, especially in the reaction range of pH 5.5 to 8.5, it is believed that the chart presents a fairly reliable picture.

*A most important point to note in the chart is that pH 6.5 is a very favorable reaction for availability of all the elements listed and obtained by plants from the soil proper. That is why, for general farming, it is usually recommended that acid soils be limed to pH 6.5. Of course, for the control of potato scab and other plant diseases and for the culture of certain ornamental plants which require a lower pH, this may not be feasible or advisable.*



## CALCIUM IN FERTILIZERS

A. L. MEHRING

*U. S. Department of Agriculture<sup>1</sup>*

The most important source of calcium in mixed fertilizers has always been superphosphate, with its high calcium sulfate content in addition to calcium phosphates. In recent years about 85 per cent of the total calcium in commercial fertilizers has been derived from this one material, 10 per cent from dolomite, 1 per cent each from calcium cyanamide and natural organics, and 3 per cent from all other materials. The average mixed fertilizer contained about 15.5 per cent CaO in most years since 1900 but has increased in recent years to approximately 17 per cent. The CaO content of mixed fertilizers is definitely related to the  $P_2O_5$  content. The CaO is at a maximum in mixtures containing about 13 per cent  $P_2O_5$ . Most of the CaO derived from dolomite is in mixtures of relatively high N and medium or low  $P_2O_5$  content. Nearly all American mixed fertilizers are abundantly supplied with calcium.

### CALCIUM CONSUMPTION

The quantities of calcium consumed in agriculture in the form of fertilizers were calculated from tonnages of the various materials consumed, as given by Mehring (15, 17), and their average CaO contents, according to Mehring and Lundstrom (14). Similar computations from the same sources were also made for liming materials for certain years from 1900 to 1929. Tonnages of the different liming materials used in agriculture from 1930 onward, however, were those published annually by the National Lime Association (18). The results are given in table 1.

Fertilizers in 1900 supplied 463,000 tons CaO, and liming materials 417,000 tons. In most of the years from 1900 to 1920, fertilizers continued to add more calcium to the soil than did liming materials. For the next 14 years, both of these classes of materials provided about the same quantities. Although the usage of both has increased rapidly in the last 10 years, liming materials now furnish about four times as much calcium as do fertilizers. In 1945 and 1946 fertilizers contained 2,531,000 and 2,740,000 tons and liming materials 9,316,000 and 12,210,000 tons of CaO, respectively. The fertilizer figures include the calcium contents of ground phosphate rock and gypsum used as sources of plant food but do not include that of gypsum used to reclaim alkali land. The figures also include the Territories of Hawaii and Puerto Rico and government-distributed fertilizers. Formerly, 85 per cent of the calcium supplied by fertilizers was in the form of mixed goods. With the increase in recent years of the use of superphosphate as a separate fertilizer this percentage declined to 60.

Fertilizers contain more calcium oxide than any other nutrient. The consumption of nitrogen in 1946 was 730,000 tons,  $P_2O_5$  1,535,000 tons, and  $K_2O$

<sup>1</sup> Division of Fertilizer and Agricultural Lime, Bureau of Plant Industry, Soils, and Agricultural Engineering, Agricultural Research Administration, U. S. Department of Agriculture, Beltsville, Maryland.



819,000 tons, making a total of 3,084,000 tons. The same fertilizers supplied 2,740,000 tons of CaO, or almost as much as the three primary nutrients combined. The total application of CaO to the soil in fertilizers and in liming materials was 14,950,000 tons, or 20 times as much CaO as N, 10 times as much as  $P_2O_5$ , and 18 times as much as  $K_2O$ .

TABLE 1  
Consumption of calcium in various forms  
In terms of 1,000 tons CaO

YEAR	FERTILIZER*			LIMING MATERIALS†
	Mixed	Separate	Total	
1900	332	131	463	417
1910	587	308	895	568
1920	917	153	1,070	1,053
1925	904	203	1,107	1,574
1929	922	360	1,282	1,583
1930	919	345	1,264	1,465
1931	713	256	969	1,096
1932	‡	‡	646	796
1933	‡	‡	743	687
1934	‡	‡	833	972
1935	725	282	1,007	1,354
1936	‡	‡	1,035	2,537
1937	998	317	1,315	2,612
1938	‡	‡	1,172	2,752
1939	825	406	1,231	3,091
1940	873	489	1,362	4,934
1941	925	617	1,542	5,844
1942	1,080	703	1,783	6,374
1943	1,208	801	2,009	6,517
1944	1,406	886	2,292	8,811
1945	1,523	1,008	2,531	9,316
1946§	1,640	1,100	2,740	12,210

\* Derived from data given by Mehring *et al.* (14, 15, 17).

† Figures for 1900 to 1929 inclusive derived from data given by Mehring *et al.* (14, 15, 17). Tonnages of materials used in calculations for later years taken from reports of the National Lime Association (18).

‡ Not available.

§ Preliminary.

#### FORMS OF CALCIUM IN FERTILIZERS

With the exception of that in raw phosphate rock, nearly all the calcium in commercial fertilizers is believed to be readily available as plant food. Considerably more than half of it is present in most cases in water-soluble forms, such as monocalcium phosphate, calcium nitrate, calcium sulfate, and calcium cyanamide. Most of the remainder is present as carbonate and the slightly soluble phosphates of bone and phosphate rock. A small part of the calcium in mixed fertilizers occurs as unaltered rock phosphate, which is fluorapatite. Some phosphate rock is added to mixed fertilizers as a filler and some as unaltered

material in superphosphate that failed to react with sulfuric acid. Very small percentages of calcium are in the form of fluoride and various silicates. Ammoniated fertilizers contain dicalcium and tricalcium phosphates and more basic phosphates formed by the action of free ammonia on the monocalcium phosphate of superphosphate.

#### SOURCES OF CALCIUM

More than a hundred different materials are used at present as commercial fertilizers. Some of these contain considerable percentages of calcium and many of the others contain small amounts. The minimum, maximum, and average CaO contents of many different kinds and grades of fertilizer and liming materials have been reported by Mehring and Lundstrom (14). The average values of some of these more commonly used materials are, according to that report, as follows:

MATERIAL	CaO CONTENT	MATERIAL	CaO CONTENT
	<i>per cent</i>		<i>per cent</i>
Bone meal, raw .....	31.40	Limestone .....	44.35
Calcium nitrate .....	27.14	Phosphate rock .....	46.29
Cal-Nitro .....	11.40	Potash-lime (5 per cent K <sub>2</sub> O) ....	45.69
Calcium cyanamide .....	53.89	Superphosphate, normal .....	27.36
Dolomite .....	30.50	Superphosphate, double .....	19.99
Gypsum .....	31.17	Wet-mixed base .....	15.83
Hydrated lime .....	62.52	Wood ashes .....	32.87

Some important fertilizers that contain little or no calcium are ammoniating solutions, ammonium phosphate, ammonium nitrate, ammonium sulfate, sodium nitrate, urea, potash salts, and organics from vegetable sources.

The principal source of calcium in mixed fertilizers, ordinary superphosphate, has supplied more than 70 per cent of the total in every year since 1900 and over 85 per cent in a few years. Dolomite provided practically none in 1920, 3 per cent in 1930, 12 per cent in 1937, and 10 per cent in 1945. Natural organics, especially bone meal and materials containing bone, such as animal tankage, fish scrap, and garbage tankage, accounted for 17.4 per cent of the total in 1900. The proportion of the total supplied by such materials has been decreasing more or less steadily ever since, so that in 1945 only 1.1 per cent came from natural organics. Calcium cyanamide furnished 4.5 per cent of the calcium in mixtures from 1925 to 1929, but the proportion declined to 1.38 per cent in 1945. All other materials put together accounted for as little as 0.8 per cent in 1900 and as much as 6.96 per cent in 1935. The most recent available figure for these miscellaneous materials is 2.96 per cent for 1945.

#### SUPERPHOSPHATES

Nearly half the total tonnage of all fertilizers consists of ordinary or normal superphosphate. It is therefore the most important fertilizer material and by far the most important source of calcium among fertilizer materials.

Results of an analysis of available calcium data relating to normal superphosphate are presented in table 2. The average CaO content of 17 samples of 18 per cent superphosphate is 27.09 per cent. The size of the standard error, 0.35, shows that the chances are 20 to 1 that the true mean of such samples is between 26.39 and 27.79 per cent. The standard deviation of 1.46 shows that about two thirds of all such samples would have CaO contents between 25.63 and 28.55

TABLE 2  
*CaO content of various grades of superphosphate*

GRADE	NUMBER OF SAMPLES*	AVERAGE AVAILABLE $P_2O_5$	CaO CONTENT				
			Minimum	Maximum	Average	Standard deviation	Standard error of mean
		<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
12-14	5†	13.23	17.00	25.82	22.46	‡	‡
16	11	16.52	22.53	29.30	25.80	1.53	.46
18	17	18.39	25.08	30.73	27.09	1.46	.35
19	1	19.17	....	....	27.42	‡	‡
20	19	20.32	26.79	30.73	28.72	1.22	.28
40-48	108§	46.74	13.22	26.40	19.71	2.34	.22
R-O-P   Fla.	38	19.63	26.23	32.15	28.70	1.20	.20
R-O-P   Tenn.	14	19.37	26.20	30.69	27.76	1.30	.35
R-O-P   West.	2	19.58	28.22	28.80	28.51	‡	‡

\* The CaO contents of 22 representative run-of-pile superphosphates that had been manufactured about 1940 by 21 different plants were provided by K. D. Jacob and W. L. Hill from unpublished analyses. Other unpublished determinations of various grades were provided at the author's request by B. W. Bellinger, U. S. Phosphoric Products Division; R. C. Charlton, American Agricultural Chemical Co.; G. M. Keller, Swift and Co.; C. C. Howes, Davison Chemical Corp.; H. L. Moxon, Virginia-Carolina Chemical Corp.; and S. F. Thornton, The F. S. Royster Guano Co. The remainder of the determinations are taken from Hardesty and Ross (4), Hart and Gary (5), Hill *et al.* (6, 7), Jensen (8), Keenen (9), Wiley (21, pt. 2, p. 71), and McCandless (11).

† Mostly from Massachusetts Agricultural Experiment Station (13). Representative of 1900 conditions.

‡ Data not suitable for calculation of these values.

§ Most of these determinations were obtained from Mehring and other sources given in his bibliography (16).

|| Run-of-pile, which means that it is not graded. The available  $P_2O_5$  of the Florida land pebble superphosphate ranged from 17.88 to 20.71, of the Tennessee brown samples from 18.10 to 21.85, and of the Western rock samples from 19.40 to 19.77 per cent. Nearly all run-of-pile samples were manufactured since 1940.

per cent. The mean CaO content of 19 samples of 20 per cent superphosphate is 28.72. The chances are equal that another group of similar samples would have a mean value between 28.44 and 29.00 and 20 to 1 that the true mean falls between 28.16 and 29.28 per cent. Run-of-pile superphosphate is used in making mixed goods. The CaO content of run-of-pile goods varies from 26 to 32, with a mean for 54 samples of goods manufactured since 1940 of 28.45 per cent. The

run-of-pile superphosphate made from Florida land pebble phosphate contains on the average about 1 per cent more CaO than that made from Tennessee brown rock. It appears from the table that as the average grade increased from that commonly used 40 years ago (12 to 14 per cent  $P_2O_5$ ) to the present-day grades (18 to 20 per cent  $P_2O_5$ ) the CaO increased from around 22 to about 28 per cent.

Double superphosphate contains, as a rule, about 19 or 20 per cent CaO. The average value for 108 samples is 19.71 per cent.

#### *Mixed fertilizers*

Many determinations of CaO in mixed fertilizers have been published. Collier (2) found an average of 17.57 per cent in three samples of material sold in Vermont in 1872. The Connecticut (3), Maryland (12), and Massachusetts (13) Agricultural Experiment Stations each have given results of CaO determinations made on two or more commercial mixtures sold between 1880 and 1903. Other analyses of that period are given by Battle (1) and by McCandless (11). These early mixtures were quite different from those sold today both in grade and in kind of materials used in their preparation. Lundstrom and Mehring (10) published complete analyses of 44 representative samples of mixed fertilizers manufactured from 1925 to 1935, inclusive. All reports of the State Chemist of Florida (20) from 1936 to 1944, inclusive, give determinations of CaO in commercial mixed fertilizers.

Some previously unpublished data are also available, including 140 determinations<sup>2</sup> on samples of representative mixed goods and a few determinations of CaO in 3-9-5 and 2-12-6 fertilizers.<sup>3</sup>

The determinations made since 1924 are assembled by grade in table 3. Of the 25 principal grades sold in the United States in 1946 all but two, 3-12-12 and 3-18-9, are well represented in this table. Some grades in the table were very popular a few years ago but are no longer manufactured.

Table 3 shows that the CaO tends to increase with the  $P_2O_5$  content to a maximum at about 12 or 14 per cent  $P_2O_5$ , although there are a few exceptions, which will be explained later.

About 92 per cent of the total tonnage of mixed fertilizers consists of grades with from 8 to 14 per cent  $P_2O_5$ , inclusive. Although nearly 300 determinations representing fertilizers from most of the states east of the Mississippi are available for such grades, only 13 contain less than 10 per cent CaO. Nearly all of these are concentrated fertilizers, such as the five samples of 12-12-21 Nitrophoska.

Table 4 summarizes 529 determinations assembled from all the sources cited above. The first five categories are complete mixtures of ordinary concentra-

<sup>2</sup> Kindly supplied by Dr. S. F. Thornton, director of chemical control of the F. S. Royster Guano Co. These mixed fertilizers were manufactured since 1943 in 13 different plants of that company scattered through Maryland, Virginia, North Carolina, South Carolina, Georgia, Alabama and Mississippi.

<sup>3</sup> Determinations made in the Fertilizer and Agricultural Lime Division of the U. S. Department of Agriculture.



TABLE 3  
CaO content of mixed fertilizers by grades\*

GRADE	PART OF TOTAL CONSUMPTION 1946	NUMBER OF SAMPLES	CaO CONTENT		
			Minimum	Maximum	Average
	<i>per cent</i>		<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
8-0-12	0.05	21	3.02	12.05	6.95
10-0-10	0.33	4	3.22	5.98	4.91
14-0-8	0.01	5	1.72	9.53	7.32
Other N-K†	0.10	10	4.62	19.60	9.52
5-3-8	0.60	5	10.80	13.20	12.09
4-4-8	0.05	4	12.92	17.81	15.71
6-4-8	0.13	7	9.12	24.75	15.37
Others with P <sub>2</sub> O <sub>5</sub> under 5‡	0.50	12	6.60	18.75	12.52
4-5-5	0.00	27	12.69	21.70	13.82
5-5-5	0.00	11	7.76	15.00	12.53
5-5-8	0.15	3	10.35	11.18	10.64
5-5-10	0.00	3	5.99	9.56	8.27
3-6-6	0.00	3	14.91	19.50	16.52
3-6-8	0.07	15	10.13	18.25	15.05
4-6-5	0.00	18	9.88	14.92	12.74
4-6-8	1.34	5	14.87	25.08	18.19
5-6-6	0.00	7	12.52	14.06	13.23
6-6-6	0.27	2	13.02	13.30	13.16
Others with 5 or 6% P <sub>2</sub> O <sub>5</sub> §	0.67	9	5.96	17.96	13.60
4-7-5	1.42	5	11.42	17.47	13.50
5-7-6	0.00	15	10.24	13.76	12.12
Others with 7% P <sub>2</sub> O <sub>5</sub>	1.74	7	10.96	19.95	13.52
2-8-10	0.03	2	12.70	17.90	15.30
3-8-5	1.63	8	9.47	16.78	14.58
3-8-8	0.29	25	9.27	21.33	15.69
3-8-10	0.00	3	7.10	17.94	12.76
4-8-3	0.00	24	9.07	20.47	16.21
4-8-4	0.08	6	13.53	16.82	15.55
4-8-6	5.28	21	15.65	18.54	16.18
4-8-8	2.95	20	13.19	19.08	16.61
4-8-12	0.79	4	15.14	17.80	16.48
5-8-7	0.45	8	11.90	16.95	13.56
6-8-4	2.78	8	18.18	19.93	18.86
6-8-6	1.94	7	17.33	19.44	18.10
6-8-8	0.62	1	....	....	18.89
6-8-16	0.00	1	....	....	8.07
8-8-8	0.33	1	....	....	8.96
Others with 8% P <sub>2</sub> O <sub>5</sub> ¶	0.56	7	12.89	19.45	16.15
3-9-6	8.18	14	15.41	18.13	16.92
3-9-9	1.73	7	16.00	18.47	17.10
4-9-3	0.85	2	16.64	16.80	16.72
Others with 9% P <sub>2</sub> O <sub>5</sub> **	2.15	6	13.82	20.17	16.11
3-10-6	0.01	2	20.41	21.03	20.72
4-10-4	1.04	6	18.00	20.84	19.98
4-10-6	5.57	11	19.35	21.69	20.12
4-10-7	2.47	14	18.71	20.97	20.10
5-10-5	6.18	12	20.03	22.04	21.03

TABLE 3—Continued

GRADE	PART OF TOTAL CONSUMPTION 1946	NUMBER OF SAMPLES	CaO CONTENT		
			Minimum	Maximum	Average
	<i>per cent</i>		<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
5-10-10	5.62	5	17.90	18.87	18.36
5-10-12	0.00	1	....	....	3.86
6-10-6	0.00	1	....	....	11.75
10-10-10	0.04	1	....	....	8.15
Others with 10% $P_2O_5$ ††	2.11	5	16.71	22.72	19.37
0-12-12	2.31	1	....	....	19.80
2-12-6	13.58	12	16.58	22.94	19.28
3-12-6	8.13	9	20.37	24.03	21.88
4-12-4	5.06	6	18.76	22.56	20.79
4-12-8	1.89	2	21.92	22.56	22.24
12-12-21	0.00	5	8.10	9.02	8.50
Others with 12% $P_2O_5$ ‡‡	5.24	4	19.35	23.52	21.02
0-14-7	1.70	2	22.04	24.82	23.43
10-15-20	0.00	2	8.49	9.06	8.78
4-16-4	0.04	1	....	....	19.88
4-16-10	0.00	1	....	....	13.29
8-16-8	0.01	1	....	....	7.29
8-16-12	0.01	1	....	....	5.20
Others with $P_2O_5$ 16 to 21%§§	1.46	1	....	....	14.58
4-24-12	0.06	1	....	....	12.89
12-24-12	0.00	1	....	....	5.85
9-27-9	0.00	1	....	....	14.58
10-30-10	0.00	1	....	....	1.91
17-34-17	0.00	1	....	....	.61
Total.....	100.00	485	0.61	25.08	15.05

\* Of goods manufactured since 1924 only; most of them since 1930. The determinations were obtained largely from three sources, as follows: Annual Reports, State Chemist of Florida (20); S. F. Thornton, in charge of chemical control, the F. S. Royster Guano Company; and Lundstrom and Mehring (10). A few additional determinations were obtained from a number of miscellaneous sources (see text). The grades are arranged in ascending order of  $P_2O_5$ . The miscellaneous grades (14-20 per cent total plant food) that are of no special significance in this study are grouped by their  $P_2O_5$  content because, as the text shows, this is of importance in connection with CaO content.

† Two samples of 8-0-10 and one each of eight other grades, none of which was reported in 1946. Average grade, 8.4-0-10.2.

‡ Average grade, 5.8-3.2-8.4.

§ Average grade, 3.9-5.9-8.7.

|| Average grade, 4.6-7-4.3.

¶ Average grade, 4-8-7.6.

\*\* Average grade, 4.5-9-5.

†† Two samples of 2-10-4 and one each of 0-10-4, 0-10-10, and 2-10-6.

‡‡ One sample each of 0-12-5, 2-12-2, 2-12-4, and 2-12-8.

§§ One sample of 3-21-6.

||| Straight average. The weighted average, using as weights the percentages of the various grades sold in 1946, is 18.69.

tion. High-analysis and concentrated grades are also grouped together. This table shows that grades containing 21 to 30 per cent total plant food contain as much calcium as those with less than 20 per cent plant food. It should be kept in mind, however, that the majority of the samples in the 21 to 30 per cent group were 4-10-7, 3-12-6, 6-12-6, 5-10-10, 4-8-12, etc., and that the average total plant-food content was only 23 per cent. In samples with 30 to 50 per cent total plant food the CaO is reduced to about half of that in the 16 to 30 per cent grades. Only three determinations were available on grades containing more than 50 per cent plant food and these were all very low in calcium.

TABLE 4  
*CaO content of various classes of mixed fertilizers*

KIND OF FERTILIZER	GUARANTEED PLANT-FOOD CONTENT	PERIOD OF TIME COVERED BY SAMPLES	NUMBER OF SAMPLES*	CaO CONTENT				
				Minimum	Maximum	Mean	Standard deviation from mean	Standard error of mean
	<i>per cent</i>	<i>years</i>		<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
N-P-K	12-20	Before 1900	16	9.96	21.25	14.11	3.14	.79
N-P-K	12-20	1900-1919	6	12.32	19.03	14.89	2.16	.88
N-P-K	14-20	1920-1929	8	5.96	17.90	15.12	4.19	1.48
N-P-K	14-20	1930-1939	160	5.74	21.70	14.49†	3.10	.24
N-P-K	16-20	1940-1947	202	5.99	29.47	16.62	3.72	.26
N-P-K	21-30	1920-1947	67	3.86	24.80	16.59	4.54	.56
N-P-K	31-40	1927-1939	5	5.20	12.89	7.86	2.74	1.23
N-P-K	41-50	1928-1941	13	1.91	14.58	7.61	3.05	.85
N-P-K	51 or more	1895-1940	3	0.30	1.18	0.70	.36	.21
N-P	14-17	1880-1900	3	14.90	15.85	15.37	.39	.22
N-K	14-28	1935-1944	38	0.20	19.60	7.09	3.39	.55
P-K	14-24	1926-1946	8	16.71	26.10	21.63	2.83	1.00

\* For source of samples see text under "Mixed Fertilizers."

† This value is believed to be about 1 per cent too low to represent general conditions in the United States, because it is heavily weighted with Florida samples, many of which are lower in  $P_2O_5$  than is typical of the country as a whole.

The ratios of calcium to the other nutrients in 4-8-4, 5-10-5, 6-12-6, 7-14-7, and 8-16-8 fertilizers, considering the nitrogen as 1, are about as follows: 4, 4, 3.5, 3, and 1, respectively.

All the samples of N-P and P-K grades listed in table 4 contain relatively large percentages of calcium. The P-K mixtures have, on the average, 40 per cent more calcium than the N-P-K grades. On the other hand, the N-K grades have only about half as much.

The first five groups in table 4 vary in the period of time in which the samples were taken. It should be noted that the average CaO for 1930-1939 is probably too low. The true average is thought to be about 15.5 or 16 per cent. The reason for this is that all samples available were used, and this average contains

an undue proportion of such Florida grades as 4-5-5, 5-5-5, 3-6-8, and 5-6-6, which are lower in calcium than typical grades for other states. As far as known, the other figures are about correct. These figures indicate that the average calcium content of mixed fertilizers has gradually increased since 1900 from about 14.5 to 17.0 per cent.

The average CaO content of all mixed fertilizers was estimated for certain years from the tonnages of materials used to make them and the average CaO content of each material. The results are shown in table 5. These figures are consistent with the data in table 4, with the exception noted above for the 1930-1939 period.

When taken together, the foregoing facts indicate that no great change has occurred in the average CaO content of mixed fertilizers, although rather radical

TABLE 5

*Average CaO content of mixed fertilizers calculated from tonnages and calcium contents of materials used to make them and by means of equations derived from analyses of samples*

YEAR	CaO CONTENT CALCULATED		
	From materials used	From curve of closest fit	
		Equation (1)	Equation (2)
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
1900	15.98	16.95	15.48
1910	14.35	16.89	15.44
1920	15.87	16.84	15.41
1925	15.57	16.95	15.48
1929	15.25	17.17	15.63
1935	15.98	16.90	15.45
1939	15.45	16.95	15.49
1941	15.96	17.08	15.57
1944	16.72	17.35	15.78
1945	17.07	17.43	15.73

changes have been made in the materials used to manufacture them. A decline in the proportion of bone has been more than compensated for by changes in the proportions derived from calcium cyanamide, dolomite, and other materials. Both sets of data indicate an upward trend in recent years.

#### RELATION BETWEEN CALCIUM AND PHOSPHORUS IN MIXED FERTILIZERS

In 1945, 92.8 per cent of the phosphorus in mixed fertilizers was furnished by normal superphosphate, and 5.8 per cent by double superphosphate, leaving only 1.4 per cent from all other sources. Inasmuch as over 80 per cent of the calcium also comes from superphosphates, it is apparent there should be a definite relationship between the  $P_2O_5$  and CaO contents of mixed fertilizers. It should be practicable to work out this relationship mathematically from analyses of samples by averaging out the fluctuations due to calcium derived from all other materials.

Normal superphosphate contains 1.45 per cent CaO for each 1 per cent  $P_2O_5$ .



Similarly each percentage of  $P_2O_5$  derived from double superphosphate carries with it 0.45 per cent CaO. Ammonium phosphates do not contain significant quantities of calcium. Therefore if the  $P_2O_5$  content and the kind of phosphate used in making a mixed fertilizer are known, the minimum CaO content may be easily computed with a fair degree of accuracy. Most commercial fertilizers, however, contain more than this minimum quantity.

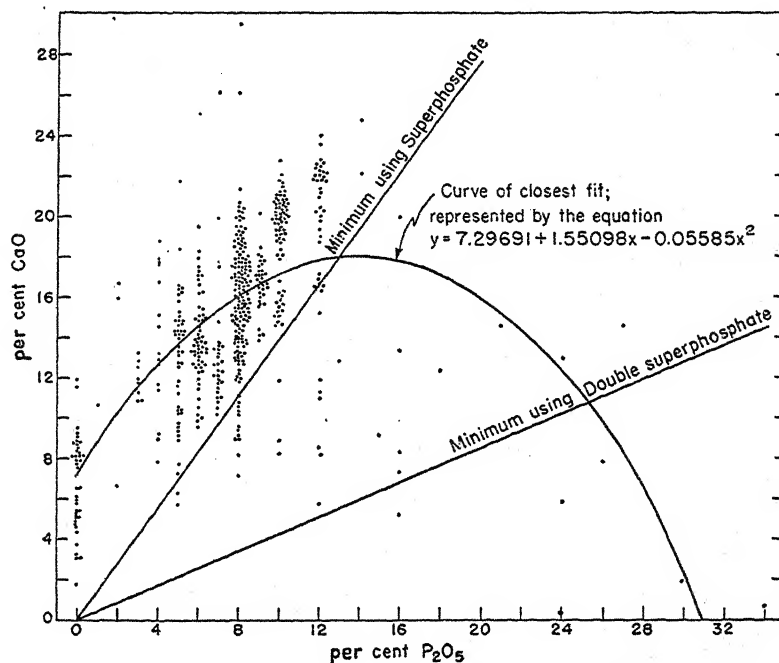


FIG. 1. THE CaO AND  $P_2O_5$  CONTENTS OF COMMERCIAL MIXED FERTILIZERS

The data represent the CaO contents found by Chemical analysis in mixtures of the guaranteed  $P_2O_5$  content indicated. The straight lines show the amounts of CaO that would be supplied by ordinary and double superphosphate at various  $P_2O_5$  levels. The dots falling below the double superphosphate line represent fertilizers deriving at least a part of their  $P_2O_5$  from ammonium phosphate. The curve was fitted to the data by least squares. A considerable part of the scatter about this curve is due to varying amounts of dolomite added to render the fertilizer non-acid-forming.

In figure 1 the actual CaO contents of 519 samples representing all types of commercial mixtures are plotted against their  $P_2O_5$  contents. The two straight lines indicate the position on the graph of the approximate quantities of CaO that correspond to the various percentages of  $P_2O_5$  when supplied by normal and double superphosphate.

It will be noted that the vast majority of all the dots representing actual determinations lie above the superphosphate line, but only a few of them lie more than 8 per cent higher. A considerable part of this additional CaO comes from dolomite and is related to the nitrogen content of the fertilizer, which will be discussed more fully in a later section.

Fourteen per cent  $P_2O_5$  in a mixed fertilizer is the maximum amount ordinarily derived from normal superphosphate alone, and this much is practical only in grades that are relatively low in nitrogen and potash, such as 0-14-7. A few unusual grades that contain only 10 or 12 per cent  $P_2O_5$ , such as 10-10-10 and 12-12-21, are manufactured, at least in part, from concentrated phosphates.

A second-degree equation that represents the curve of closest fit was calculated by the method of least squares from the 519 pairs of suitable CaO and  $P_2O_5$  determinations on mixed fertilizers available in this study. The resulting equation is as follows:

$$y = 7.29691 + 1.55098 x - 0.05585 x^2 \quad (1)$$

when  $y$  is the CaO and  $x$  the  $P_2O_5$  content. By setting the first derivative of this function equal to 0 and solving, it was learned that the maximum value of  $x$  occurs when  $y$  equals 13.89. Thus under the average conditions of the data used in deriving the equation, the maximum possible CaO content occurs when the  $P_2O_5$  content is 13.89. This point corresponds to 18.06 per cent CaO. It is almost exactly the point at which the superphosphate line intersects the curve of closest fit in figure 1. This shows mathematically what many persons have learned from experience; namely, that it is necessary to employ double superphosphate or ammonium phosphate for at least a part of the  $P_2O_5$  in order to manufacture mixed fertilizers of ordinary plant-food ratios containing more than 12 per cent  $P_2O_5$ , or 25 per cent total plant food.

The double superphosphate line intersects the curve at a point corresponding to 25 per cent  $P_2O_5$ . Ammonium phosphate must be used to manufacture mixed fertilizers of normal ratios with more than 25 per cent  $P_2O_5$ . The minimum CaO percentage corresponding to this value is 11.17. The CaO content drops very rapidly as the  $P_2O_5$  increases above this point. It reaches zero at 31.87 per cent  $P_2O_5$ . The highest practical  $P_2O_5$  content with a 1-2-1 ratio of plant nutrients is about 34 per cent.

Equation (1) was used to compute the CaO content of all mixed fertilizers consumed in the years given in table 5. The equation gives somewhat higher results than were obtained from the tonnages of materials used to manufacture them. This may indicate that the sample population used to derive the equation contained an unduly high proportion of individual samples that were too high in calcium to be exactly representative.

The Royster Guano Co. is one of the few fertilizer manufacturers that regularly guarantee the CaO content of their mixed goods. The fact that they guarantee it may indicate higher than usual percentages. Inasmuch as a very large number of the samples were of this company's manufacture, a new equation was fitted by least squares to the data for the 379 samples of other manufacturers' goods. The new equation is as follows:

$$y = 8.3285 + 1.1965 x - 0.0464 x^2 \quad (2)$$

This equation also was used to calculate the average CaO content of mixed fertilizers used during certain years. The results are in the right-hand column of

table 5. These data agree much better with the figures obtained from the materials used to make mixed fertilizers in the years up to and including 1939 but are too low for the succeeding years.

TABLE 6  
*CaO content of mixed fertilizers of varying available  $P_2O_5$  content*

$P_2O_5$	NUMBER OF SAMPLES	EXPERIMENTAL CaO CONTENT			CALCULATED CaO CONTENT		
		Mean CaO	Standard deviation from mean	Standard error of mean	From equation (1)*	From super- phosphate†	Difference‡
1	2	3	4	5	6	7	8
<i>per cent</i>		<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
0	39	6.75	2.34	0.38	7.29	0	7.29
2§	4	12.44	4.12	2.06	10.18	2.90	7.28
3	8	11.89	2.44	0.86	11.45	4.35	7.10
4	15	13.72	3.49	0.90	12.61	5.80	6.81
5	47	12.89	3.18	0.46	13.66	7.25	6.41
6	58	14.26	2.66	0.35	14.59	8.70	5.89
7	28	13.22	3.18	0.60	15.42	10.15	5.27
8	157	15.90	2.48	0.21	16.13	11.60	4.53
9	33	16.76	1.22	0.21	16.73	13.05	3.68
10	72	18.80	2.79	0.33	17.22	14.50	2.72
12	41	18.90	4.58	0.72	17.87	17.40	0.47
14	4	17.17	6.41	3.20	18.06	17.70	0.36
16	5	10.78	5.27	2.35	17.81	17.50	0.31
18	1	12.32	....	....	17.12	16.80	0.32
24¶	6	9.33	5.22	2.13	12.35	12.00	0.35
30	1	1.91	....	....	3.56	3.20	0.36
34	1	.61	....	....	0	0	0

\*  $y = 7.29691 + 1.55098x - 0.05535x^2$ , which was derived by least squares from 519 determinations on representative samples, where  $y$  = CaO content and  $x$  =  $P_2O_5$  content of sample.

† From the quantities of the respective grades of superphosphate estimated to be used to manufacture grades of such  $P_2O_5$  content, assuming that run-of-pile superphosphate containing 1.45 per cent CaO for each 1 per cent  $P_2O_5$  is used for  $P_2O_5$  contents up to 12, varying proportions of normal and double superphosphate for grades containing from 14 to 24 per cent  $P_2O_5$ , and increasing percentages of ammonium phosphate for grades containing more than 24 per cent  $P_2O_5$ .

‡ Column 6 minus column 7.

§ Including 1 sample of 1 per cent  $P_2O_5$  content.

|| Including all samples from 13 to 15, inclusive.

¶ Including all samples from 21 to 27, inclusive.

The mean CaO contents of all samples of each  $P_2O_5$  content are listed in table 6.

Equation (1) was also employed to determine the average for each group, and the results are given in column 6 of the same table. The latter agree reasonably well with the experimental means in column 3. The standard deviation from the curve is 3.47.

The curve of closest fit is the best estimate of the average relationship from the

available data. Another collection of samples would give a slightly\* different curve of the same general relationships. The statements in the preceding paragraphs of this section of the paper are to be construed as applying approximately to normal or average conditions. Unimportant exceptions may be found quite readily that do not agree with the general principles outlined.

#### RELATION BETWEEN CALCIUM AND NITROGEN IN MIXED FERTILIZERS

In the previous sections it was shown that most of the calcium in mixed fertilizers comes from superphosphates. Comparison of columns 6 and 7 of table 6 shows, however, that just the reverse is true when the  $P_2O_5$  is low. If superphosphates were the only sources of calcium, there would be none in top-dresser fertilizers, such as 8-0-12, and yet the average CaO content of 39 samples of such fertilizers is 6.75 and the least squares equation indicates that they should contain an average of about 7.29 per cent. This calcium comes from various materials, but principally from dolomite. The figures in column 8 show that these other materials supply much calcium when the phosphorus is low and very little when the  $P_2O_5$  content is 12 per cent or higher. This is related to the nitrogen content, which in turn is related to the  $P_2O_5$  content.

If the first number in a grade formula is high, the second is usually relatively low; for examples, 10-0-10, 8-4-8, and 10-6-4. On the contrary, when the nitrogen is low, the  $P_2O_5$  is generally high, as in 2-12-6 and 0-20-20.

The more nitrogen a mixed fertilizer has in it, the more acid-forming it will be, other things being equal. Consequently more dolomite is likely to be added to mixed goods of high nitrogen content. A few examples will make these statements clear.

No calcium-containing material, except superphosphate and a little hydrated lime to neutralize the acid properties of the superphosphate, is necessary in the manufacture of P-K mixtures such as 0-9-27 and 0-14-14. A few P-K grades, like 0-12-6, however, are exceptions to the general rule and contain dolomite as a filler. If relatively little nitrogen in proportion to  $P_2O_5$  is used in a formula, as in a 2-12-6 fertilizer, ammonia solutions can supply all the nitrogen. In such a case the fertilizer is only acid-forming to the extent of requiring 72 pounds of limestone per ton to neutralize it. The 2-12-6 is the most popular grade in the United States. The bulk of this, as well as of P-K grades, is consumed in the North Central region where most soils are regularly treated with heavy applications of ground limestone. In this region slightly acid-forming fertilizers are not objectionable, and relatively little dolomite is used as filler. Thus in most cases grades containing little or no nitrogen will contain little calcium from any source other than superphosphate.

On the contrary no ammonia can be utilized in the manufacture of grades like 10-0-10 and 8-0-12. Only a small part of the nitrogen required in grades like 6-8-4 and 10-6-4 can be furnished by ammoniating solutions. Thus in the preparation of such grades, materials more acid-forming than ammonia, such as ammonium sulfate, are customarily used as sources of nitrogen. As the proportion of nitrogen to phosphoric acid in a mixed fertilizer goes up, therefore,

relatively more dolomite is needed if non-acid-forming fertilizers are desired. For example, if ammonium sulfate is used as the source of nitrogen in a 10-0-10 fertilizer, nearly 1,100 pounds of dolomite would be required to make it non-acid-forming. Although it is impossible to add that much, such mixtures usually contain 5 to 10 per cent of CaO in the form of dolomite. The samples of mixed fertilizers used in this study having less than 22 per cent total plant food contain on the average 1.14 per cent CaO for each 1 per cent nitrogen in addition to the 1.45 per cent for each 1 per cent of  $P_2O_5$ . As a rule, the samples of higher total plant-food content than 30 per cent contain only a fraction of 1 per cent more CaO than can be accounted for by the calcium content of the phosphates that must have been used in their preparation.

#### CALCIUM IN FERTILIZER APPLICATIONS

The quantities of CaO contained in fertilizers added to various crops in the year 1944 are listed in table 7. The sources of information are given in footnotes to the table.

Column 7 of table 7 shows that the calcium content of the kind of fertilizers applied to different crops varies from about 10 per cent for onions to about 22 per cent for hay. The high percentage for hay is due to the fact that a large part of the fertilizer applied to this crop is straight superphosphate. The high value for 42 other crops is due to the large quantity of fertilizer applied to pastures in the soil conservation program. Most of this pasture fertilizer also consists of superphosphate. Large quantities of straight sodium and ammonium nitrates are applied to cotton and cabbage. This tends to lower the averages, especially for cotton, which otherwise would be high because of the large amounts of dolomite used in the manufacture of most grades of mixed fertilizers for this crop.

The average rate of application of calcium in the form of fertilizers was worked out both on the basis of all land in that crop in 1944 and on the basis of the rates of fertilizer application actually found in the Third Fertilizer Practices Survey of the National Fertilizer Association. Much more calcium is added to each acre of some crops than of others. Most is added to tobacco and vegetables and least to grains and cotton.

Columns 8 and 9 of table 7 show that much more calcium is added per acre to some crops on the basis of the Third Survey than when the total tonnage is averaged equally for every acre of that crop in the United States. This difference is particularly noticeable for hay, corn, wheat, oats, and 42 other crops. The reason for the large difference in application rates is that much of the land devoted to grain and hay crops received little or no fertilizer. This unfertilized land naturally was largely unrepresented in the National Fertilizer Association Survey.

For comparison, the CaO content of the harvested portion of the various crops is set forth in column 10. This is calculated on the basis of the actual yields in 1944 as published in Agricultural Statistics. Although the quantities of calcium removed from the soil by crops are small in most cases in proportion to the quan-



TABLE 7

Calcium oxide contents of fertilizer applications and harvested portions of crops, 1944

CROP	AVERAGE ACRE YIELD*	HARVESTED LAND*	FERTILIZER CONSUMPTION†	AVERAGE APPLICATION RATE		CaO CONTENT OF			
				All land‡	NFA Survey§	Average fertilizer application			Harvested crop¶
						Estimated	All land¶	NFA Survey**	
1	2	3	4	5	6	7	8	9	10
		1000 acres	1000 tons	lbs./acre	lbs./acre	per cent	lbs./acre	lbs./acre	lbs./acre.
Tobacco...	1,117 lbs.	1,752	796	909	1,265	13	118	164	61.4
Hay.....	1.32 tons	74,016	952	26	488	22	6	107	24.2
Peanuts...	670 lbs. nuts, 1½ tons hay	3,999	209	105	444	17	18	75	21.4
Corn.....	33 bu. grain, 1 ton stover	97,078	2,909	60	365	15	9	55	13.5
Onions....	262 bu.‡‡	179	46	514	1,098	10	51	110	7.2
Cabbage...	6.35 tons	219	105	959	1,200	12	115	144	7.0
Wheat....	18 bu. grain, 1 ton straw	59,095	1,044	35	295	17	6	50	5.9
Oats.....	30 bu. grain, 1 ton straw	38,735	665	34	357	18	6	64	5.2
Cotton...	294 lbs. lint, 490 lbs. seed	20,009	1,631	163	338	14	23	47	0.9
Potatoes..	131 bu.	2,922	900	616	1,860	13	80	242	0.7
42 others..		52,976	3,788	143	686§§	21	30	144	14.9
Total or Average.....		350,980	13,045	74	626¶¶	17	13	106	13.3***

\* From Agricultural Statistics 1946. U. S. Dept. Agr. The corn stover and straw are estimated.

† Estimated from the 1942 figures given by H. R. Smalley and R. H. Engle, *Fert. Rev.* 18 (3): 3, 1943.

‡ Computed from data in columns 3 and 4.

§ The weighted averages of the state figures given in the Third National Fertilizer Practice Survey, 1944. National Fertilizer Association, 1946.

|| Estimated from the kinds and grades of fertilizers shown by the Third Fertilizer Practice Survey to have been used in 1944 on each crop and the CaO contents of those fertilizers. The total is calculated from the materials used as fertilizers in 1944 and their CaO contents. The figure for all other crops is estimated by inserting in this category all calcium not accounted for in columns 4 and 7.

¶ Computed from data in columns 5 and 7.

\*\* Computed from data in columns 6 and 7.

‡‡ Computed from average yields in column 2 and Ca contents given by Beeson in U. S. Dept. Agr. Misc. Pub. 369, 1941, corrected from the dry basis to the moisture content customary in commerce.

§§ 50-pound bushels.

§§ Sweet potatoes 1,577, barley 381, fruits and nuts 1,064, soybeans 341, other vegetables 1,251, all other crops 431.

||| 52 principal crops; adjusted to eliminate duplication.

¶¶ Weighted average, using the data in column 4 as the weights.

\*\*\* Average weighted by data of column 3.

ties applied in fertilizers, the picture is complicated by additional applications in the form of liming materials and farm manures and by relatively large losses by the leaching effect of rain water with carbon dioxide in solution.

#### CONCLUSIONS

Fertilizers contain a larger percentage of calcium than of any other single nutrient. In fact, the CaO content is almost as large as the sum of the N,  $P_2O_5$ , and  $K_2O$  contents.

The average CaO content of all fertilizers sold in recent years to American farmers is about 17 per cent. Less than one tenth of the total tonnage of all fertilizers consists of materials essentially lacking in calcium, such as certain nitrogen and potash salts. The use of these low-calcium materials unmixed is largely confined to the top-dressing and side-dressing of crops that have already received liberal applications of mixed fertilizers well supplied with calcium.

Nearly all brands and kinds of mixed fertilizers sold in substantial tonnages contain 10 per cent or more of CaO. The average CaO content of all mixed goods sold in recent years is about 17 per cent, that of normal superphosphate about 28 per cent, and that of double superphosphate approximately 20 per cent.

Mixed fertilizers, the plant-food ratio of which is high in  $P_2O_5$ , like 2-12-6, are usually high in CaO also. Such fertilizers derive most of their calcium from the calcium sulfate and calcium phosphates in superphosphate. High-nitrogen mixtures such as 8-0-12 and 10-6-4 obtain their calcium principally from the calcium carbonate in dolomite. Inasmuch as all important commercial sources of fertilizer potash are low in calcium, there is no relationship between the potassium and calcium contents of mixed fertilizers.

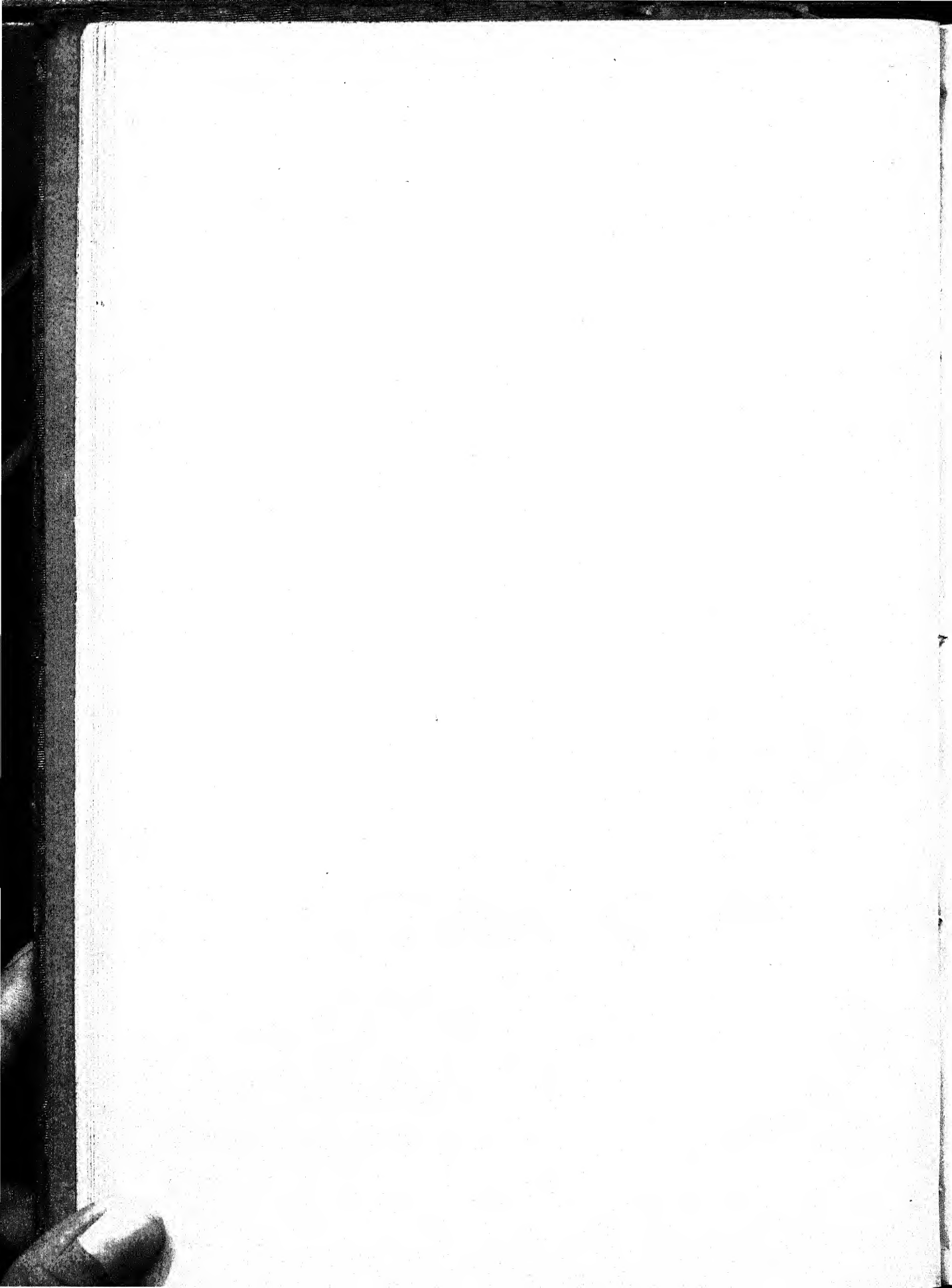
The calcium content of mixed fertilizers is related to the total plant-food content. It increases with the concentration of plant food to a total of about 25 per cent, when it decreases gradually at first and then rapidly. Although mixed goods can be prepared with a combined total of N,  $P_2O_5$ , and  $K_2O$  as high as 65 or 70 per cent, none of those examined that totaled over 50 per cent contained more than 2 per cent CaO.

The calcium content of fertilizers varies according to the crop on which the fertilizer is used. The quantities of calcium applied per acre also differ widely with various crops. For most crops, far more calcium is applied to the land than is removed from it in the harvest.

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## DIFFERENTIAL EFFECTS OF VARIOUS CALCIUM CARRIERS UPON TRANSITIONS IN PHOSPHATE MIXTURES

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This paper is intended as a resumé of some of the findings and conclusions resultant from studies conducted during three decades at the University of Tennessee Agricultural Experiment Station, and the observations relate almost exclusively to experiments from that source (1-24).

Interest as to inclusion of basic materials in phosphatic fertilizers was responsive to queries and concern about the admissibility and compatability of different forms and proportions of calcic, magnesian, and dolomitic materials. It seemed feasible to displace sand filler through the incorporation of nutrient materials that would impart to fertilizers an improved mechanical condition, protect the bag-containers against chemically induced disintegration, and also provide a supplement of magnesium to superphosphates and mixed fertilizers through the innixing of dolomite.

On the basis of laboratory studies on the relative dissolubilities of various types of limestone, it appeared probable that incorporation of dolomite would not impart appreciable alkalinity to superphosphate. The inclusion of dolomite in superphosphate and mixed fertilizers was recommended, therefore, to two manufacturers in 1919, and the proposal was implemented by a Tennessee manufacturer shortly afterward. The subsequently published small-scale studies of superphosphate-limestone and superphosphate-dolomite mixtures were based upon progression in the evolutions of  $\text{CO}_2$  from mixtures under various conditions as to proportions, moisture content, and particle size. The findings served to demonstrate the quick attainment of pseudoequilibrium, in the mixtures of limestone and of dolomite, in the formation of binary phosphates, under ordinary moisture content. It was established that superphosphate can be mixed to advantage with either type of dry limestone, without appreciable percentage formation of citrate-insoluble phosphates, when the bulk of the mixtures is restricted after the mixings. The dual reactions between the Ca and Mg of dolomite and the water-soluble phosphate content of superphosphate were more desiccative than the corresponding reaction induced by limestone. It was concluded that the ultimate phosphorus conversion in the limestone mixtures was the anhydride of the secondary calcium phosphate, whereas that form and the hydrated form of dimagnesium phosphate were generated in the dolomite mixtures.

Even when the limestone proportions were multiple, there was no development of tertiary phosphate during storage of the dry mixtures. In some such cases, however, decreases in  $\text{P}_2\text{O}_5$  availability were registered by analysis, because of the dissolving of the basic components engendered during the citrate digestion of the water-insoluble phosphates and of the residues of the limestone, and because of the induced elevation in the pH of the solvent and resultant diminished dis-



solvent effectiveness. The rapid conversion to dicalcium phosphate in continuously agitated aqueous suspensions of limestone and superphosphate was followed very slowly by the ultimate displacement of only three fourths of the third potential hydrogen. But, in corresponding suspensions of superphosphate and dolomite, the potential reactions were virtually at a standstill after the binary phosphates had been generated.

In related further studies, measurement of the  $\text{CO}_2$  evolutions from aqueous suspensions of superphosphate and limestone, and of dolomite, and determinations of concomitant solute phases were utilized to show that neither tricalcium nor trimagnesium phosphate is formed in aqueous systems of initial monocalcium phosphate content and an excess of dolomite. In such suspensions, solute  $\text{MgH}_4[\text{PO}_4]_2$  proved inert toward 325-mesh dolomite, and that component also inhibited reaction between solute monocalcium phosphate and dolomite in aqueous suspensions. Both of the monophosphates did react with dolomite, however, in thick slurries.

A progression of analyses of the undecomposed fractions of the inmixed limestone served to establish the fact that the reaction between dicalcium phosphate and limestone was sluggish in periodically wetted mixtures; and, even after 13 months, transition to the tertiary form was only 60 per cent of the potential, against a 20 per cent transition induced by dolomite in corresponding mixtures during that period. In related work, it had been found that the synthetic ammoniacal phosphates could be protected against hygroscopicity, without loss of ammonia or decrease in  $\text{P}_2\text{O}_5$  availability, when either dry limestone or dry dolomite was admixed in substantial proportions.

When 10-ton lots of 1 + 2 mixtures of concentrated superphosphate and wetted limestone or wetted dolomite were stored 30 days in wooden bins, setting occurred and phosphorus availability decreased only in the center of the bin-enclosed piles of limestone mixtures, whereas caking was less and there was virtually no loss of  $\text{P}_2\text{O}_5$  "availability" in the dolomite piles. When similar wetted dilutions of concentrated superphosphate were turned by shoveling in small piles, there was no lumping or set-up. The moist mixtures also attained good mechanical condition when they were placed immediately in bags, incompletely filled, and the partly filled bags were up-ended several times during 2 or 3 successive days. Under these conditions, the development of dicalcium phosphate reached 90 per cent of that possible in the limestone mixtures, against an 80 per cent transition to dicalcium and dimagnesium phosphates in the dolomite mixtures.

Wetting of the limestone and dolomite to expedite the generation of dicalcium phosphate or the dual formation of dicalcium and dimagnesium phosphates was prompted by the determined stability of dicalcium phosphate in contact with limestone and by the Neubauer findings that rye seedlings had a much larger uptake of phosphorus from dicalcium phosphate than from water-soluble calcium phosphate. Those tests showed that, in a prelimestoned soil, monocalcium phosphate incorporations passed quickly into the dicalcium form and that the judicious preliming tended to prolong occurrence of dicalcium phosphate in the soil system.

From the several observations as to the superiority of wollastonite over equivalent quantities of limestone and effects induced by incorporation of the calcium carbonate in phosphatic fertilizers, it was postulated that appropriate admixtures of calcium silicate would exert two effects upon concentrated superphosphate. It was found that, although acidulations of rock phosphate by means of 35 per cent  $\text{H}_3\text{PO}_4$  give slurries that are permanent, the slurries could be converted into substantially desiccated mixtures as the joint effect of generated dicalcium phosphate and hydration of the silica released from the reaction between the acidic phosphates and 10 to 15 per cent additions of calcium silicate, either the mineral form or that of *blast furnace slag*, although the slag from the rock phosphate reduction furnace is not admissible because of its content of fluorine. The induced mechanical change from slurry to thick paste was such as to admit of the belt-conveyance of the mixtures in drying operations, and the process was covered by U. S. Patent No. 2,086,565, "Making Calcium Phosphate Fertilizer."

The admixing of either limestone or dolomite facilitates handling of calcium metaphosphate at point of usage. This product of 65 per cent  $\text{P}_2\text{O}_5$ -equivalence is virtually a dehydrated monocalcium phosphate that keeps fairly well while in lumps. When ground, however, it undergoes hydration and caking, even when in heavy paper containers. The hygroscopic tendencies of finely ground calcium metaphosphate were found to be overcome completely in its mixtures with three parts of limestone or of dolomite, even after 1-ton mixtures had been aged 3 months in the open.

Introduction of readily reactant calcium along with an active form of  $\text{MgO}$  was effected by the use of dolomite that had been calcined selectively to a composition of  $\text{CaCO}_3 \cdot \text{MgO}$ , with meager concomitance of  $\text{CaO}$ . Such a product was obtained by carefully controlled calcination of dolomite of admissible sizing at  $725^\circ\text{C}$ . A material characterized by particularly active calcium carbonate and magnesium oxide was obtained, however, through calcination of dolomite in a current of steam at  $600^\circ\text{C}$ . Admixtures of 10 to 20 per cent of the  $\text{CaCO}_3 \cdot \text{MgO}$  calcine exerted beneficial mechanical effects upon superphosphate and induced rapid transitions of its water-soluble phosphates to dicalcium and dimagnesium forms, and also to magnesium-ammonium phosphate in phosphatic fertilizers that contained ammonium sulfate, and without attendant  $\text{P}_2\text{O}_5$  retrogradation. Since the  $\text{CaCO}_3$  of the selectively calcined dolomite is in a form comparable to that of precipitated calcium carbonate, and since the concomitant  $\text{MgO}$  is unusually reactant, the reactions between the water-soluble phosphate of superphosphate and the Ca and Mg components of the calcine can be induced preferentially to almost full extent when moisture conditions are varied in range between those of ordinary mixtures and those of slurries.

Because of its ready reactivity, quenched calcium silicate slag was mixed with concentrated superphosphate in the dry state, as had been done with limestone and with dolomite. When added in 2 to 1 proportion, the slag served to convert some 30 per cent of the water-soluble phosphate to dicalcium phosphate, with an attendant desiccation that brought reaction to a standstill without loss of  $\text{P}_2\text{O}_5$  availability. But, when the slag was wetted before its admixture, in the same

manner as the limestone and dolomite had been wetted to advantage in their respective 2 to 1 mixtures with superphosphate, the larger fraction of the initial water-soluble phosphate was rendered *citrate-insoluble* during the periods of 1 week and 1 month. A followup study served to establish the validity of the postulation that tricalcium phosphate had been engendered by the relatively avid slag and that the generated tertiary phosphate reacted with the component fluoride of the superphosphate, and/or with the much larger proportion of fluoride that was liberated through the hydrolytic disintegration of the slag, with resultant formation of the fluorophosphate equivalent of apatite. Subsequent findings have indicated that the fluorine liberated during hydrolysis of the slag is in the form of silicofluoride rather than calcium fluoride.

In further studies with calcium-fortified superphosphates, it was demonstrated that the component fluoride induced formation of calcium fluorophosphate, whether the fluoride was contained in the superphosphate or in the added calcic material. When experimentally produced fluorine-free superphosphates were used in mixtures of admissible bulk with limestone, dolomite, or calcium silicate, citrate-insoluble  $P_2O_5$  did not develop. No recognition had been accorded the potency of the 3 to 4 per cent calcium fluoride content of superphosphate as a factor in the diminution of  $P_2O_5$ -availability in ammoniated mixtures of superphosphate and dolomite. The nearest approach to such recognition was the citation by Frank G. Keenen<sup>1</sup> to the effect that the tertiary phosphates engendered in the ammoniation of superphosphate were considerably less soluble than the precipitated tricalcium phosphates of the laboratory. Moreover, it was found that heavy-rate ammoniation of superphosphates resulted in development of tertiary calcium phosphates which reacted with the fluoride component of the superphosphate and formed fluorophosphate, without additive lime.

In a number of trials *blast furnace* fluoride-free slags were used in lieu of wollastonite, when desiccation of the slurried systems was the objective. That slag was found effective and compatible, the one objection to its use being the evolution of hydrogen sulfide that occurs when it is mixed with the slurry of superphosphate.

The potential reaction between calcium fluoride and tertiary calcium phosphate in alkaline systems in ordinary temperature range should have been reasoned from the substantial immediate decrease in the proportion of available  $P_2O_5$  in basic slag that is processed by an input of fluorspar to impart greater fluidity to the molten draw. After the reaction between superphosphate and the quenched calcium silicate slag output from the rock phosphate reduction furnace had been explored, it was postulated that the same reaction could be implemented to effect removal of fluorides from natural waters. The subjective tests and the findings resultant from that postulation did eventuate into U. S. Patent No. 2,126,793, "Removing Fluorides from Water."

Unexpectedly, the postulated formation of fluorophosphate in calcium-fortified superphosphate was encountered by Beeson and Jacob<sup>2</sup> when they incorporated

<sup>1</sup> *Indus. and Engin. Chem.* 22: 11. 1930.

<sup>2</sup> *Indus. and Engin. Chem.* 30:304-308. 1938.

a fluoride-free form of tricalcium phosphate (a powdery form of defluorinated rock phosphate) into mixtures of superphosphate and ammonium sulfate. They sought to ascertain whether the powdery phosphate induced any loss of ammonia from the included ammonium sulfate, and found that restriction in the proportion of the defluorinated phosphate was necessary to avoid that loss. They also encountered a decided percentage decrease in occurrence of available  $P_2O_5$  in their experimental mixtures. When their experiment was simulated *in toto*, plus the inclusion of a superphosphate prepared from a completely defluorinated fused tricalcium phosphate, our findings duplicated theirs. But citrate-insoluble  $P_2O_5$  did not develop in the supplemental systems that comprised the experimental superphosphate and the virtually defluorinated rock phosphate powder, both of which were almost devoid of fluorine. In a subsequent study, the foregoing tests were duplicated, except for substitution of finely ground fused tricalcium phosphate, a crystalline product comprised chiefly of the alpha form, in lieu of the powdery defluorinated rock phosphate. The fused material proved mechanically compatible for admixing with unaltered superphosphate, and with superphosphate that contained ammonium sulfate, and did not induce the development of citrate-insoluble  $P_2O_5$  that had resulted from corresponding usage of the powdery defluorinated rock phosphate.

Since the incidence of fluorine, both component and additive, appeared to exert such a detrimental effect upon the availability of the  $P_2O_5$  content of the calcium-fortified mixtures of superphosphate, and since the mixing of powdery calcium fluoride with precipitated tricalcium phosphates outside the soil caused such a marked decrease in  $P_2O_5$  solubility, as such was measured by chemical procedures and by seedling uptake in Neubauer tests, the question arose as to whether calcium fluoride incorporations would exert a like effect upon binary and tertiary calcium phosphates in soils moderately limed, when the fluoride and phosphate materials were separately incorporated. From trials with 35 such soils, into which precipitated  $CaF_2$  was incorporated later, it was found that uptake of phosphorus from the directly incorporated tertiary phosphate was decidedly less than uptake from the parallel incorporation of dicalcium phosphate. This afforded additional indication of the desirability of effecting a soil system in which the preferred form of dicalcium phosphate is generated, and under conditions that prompt its persistence as a soil component.

Although mixing of the quenched slag with superphosphate caused marked decreases in plant response to such mixtures when they were allowed to age before incorporation, there was no such detrimental effect when identical mixtures of the slag and superphosphate were incorporated immediately or when the separate materials were incorporated simultaneously. In most cases, an incorporation of the quenched slag induced plant response beyond that induced by an equivalence of limestone plus superphosphate in equivalence to the phosphorus content of the slag, and the joint addition of superphosphate and slag proved more effective than a like combination of superphosphate and limestone.

In further studies, the objective was to ascertain whether cumulative inputs of calcium fluoride would develop a built-up oil content of fluorine that might



affect the availability of phosphorus carried by incorporations of superphosphate. A normal superphosphate and an equivalence of fluoride-free monocalcium phosphate were incorporated, in parallel, in quantities equivalent to 500 single incorporations of standard superphosphate. The effect of the acidity of such a heavy incorporation of monocalcium phosphate was eradicated through a corrective 20-ton supplement of calcium silicate. The large input of the component fluoride induced no harmful effect, and there was no substantial increase in uptake of fluorine.

Since there was a decided difference between the reactivities of the quenched glassy slag and the air-cooled crystalline slag from the same rock phosphate furnace, the question arose as to whether the transient toxicity induced by heavy incorporations of finely ground quenched slag could be attributed to the concomitant increases in the inputs of fluorine. Therefore, fluorspar and precipitated calcium fluoride were incorporated in quantities respectively equivalent to 2 tons and 4 tons of  $\text{CaCO}_3$  per acre, and three successive crops were grown in pot cultures. The fluorides exerted no detrimental effect upon germination, and they did not promote plant growth. Both of the fluorides proved inadequate as a source of nutrient calcium, and both exerted a repression upon the availability of the additions of superphosphate that were made before seeding of the third crop, which was alfalfa. Slight elevations in pH values were induced by both fluoride compounds.

A qualification should be made as to the reactivity and beneficial effects of quenched calcium silicate slag from electric furnaces, when that slag is used jointly with superphosphate. When derived from reduction of rock phosphate high in clay content, a slag will have an undue content of alumina, which promotes formation of gehlenite, incidence of which diminishes greatly the liming value of the slag and serves to inactivate its contained phosphate, even when the quenched slag is pulverized.

As an over-all integration of the several findings, it is concluded that superphosphate can be benefited mechanically and chemically by inclusions of rational quantities of calcium in the several forms of limestone, dolomite, and selectively calcined dolomite, when bulk is so restricted and so handled as to prevent rise in temperature, and provided the inmixed materials are in such proportion as not to induce undue "C.I." values when the processed phosphatic mixtures are subjected to the official analytical procedures. A like conclusion appears justified for moderately dry mixtures of slags and concentrated superphosphate when the slags are of admissible type and composition, and when the resultant transformed mixtures are channelled to immediate incorporation. The desirable transition to the binary phosphates that are engendered by the admixing of wetted limestone and wetted dolomite with concentrated superphosphate, can be effectuated quickly and without detriment to  $\text{P}_2\text{O}_5$  availability, as measured chemically, when the wetted mixtures are kept within reasonable bulk and are so handled as to preclude development and persistence of an elevated temperature in the piles.

One virtually invariable result has been that, under all conditions, calcium



metasilicate has proved superior to equivalent quantities of calcium carbonate in direct comparisons as liming materials and when in association with superphosphate. The silica content of wollastonite and of the slag forms of calcium silicates seems to have a value in its relation to the phosphate nutrition of the plant, and currently reported findings indicate that leaching of slag-derived solvated silica may promote leachability of concomitant occurrences of fluorine.

Apparently, no detrimental effects can be attributed to reactions that ensue between the component fluoride of calcium silicate materials and the component phosphate of superphosphate after they are incorporated, either separately or jointly. There is some evidence that the component fluorine of conventional phosphatic fertilizers exerts a beneficial influence upon plant growth, and currently reported experiments show that virtually all such input of fluorine was retained by the soil against rain-water leachings from a 51-inch annual precipitation during 10 years.

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## CHEMICAL METHODS FOR ESTIMATING LIME NEEDS OF SOILS

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Many different chemical methods for determining lime needs of soils have been proposed and are now in common use. These vary from simple, qualitative, and indirect tests to more quantitative and direct lime-requirement methods and involve determination of exchangeable hydrogen, exchangeable calcium, degree of calcium saturation, soil reaction, or amount of readily soluble aluminum, iron, and manganese present in the soil. Of the chemical methods, the soil reaction test (pH) is used most widely and is perhaps easiest to make. Determination of exchangeable hydrogen either by direct potentiometric titration of the soil or after extraction with some salt solution is the basis of the more quantitative lime-requirement methods designed to measure how much  $\text{CaCO}_3$  must be applied to a given soil to bring the reaction to neutrality or to some other desired pH value.

The better lime-requirement methods are based on sound chemical principles and are capable of determining rapidly and accurately the amount of lime needed to bring the soil reaction to some arbitrary pH value. Translation of the results of the tests into the most economical amount of lime that needs to be applied to a given soil for optimum growth of a certain crop is, however, a much more difficult task. This is because we do not have a thorough understanding of the fundamental causes of poor growth of plants on acid soils. Indeed, there is little agreement today among soil and plant scientists as to the fundamental factors involved in the responses of different crops to applications of lime on acid soils. Not until the relative importance of the different beneficial effects of lime on different acid soils is accurately known, will it be possible to evaluate the chemical methods for estimating lime needs of soils.

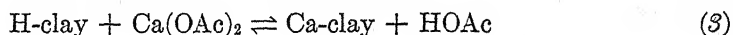
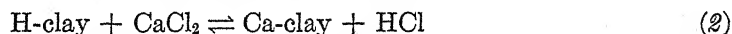
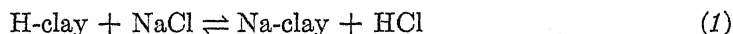
Critical examination of the different kinds of chemical methods that have been proposed for estimating the need for liming soils should, nevertheless, prove to be of value. That is the purpose of this paper. Because of space limitations, only the more common and promising methods are reviewed. The methods are not described in detail, but the principles upon which they are based, the important inherent sources of error in them, and their relative usefulness in liming recommendations are discussed. The methods are considered under the following headings: (a) determination of exchangeable hydrogen; (b) rapid determination of the lime requirement; (c) determination of soil reaction; (d) determination of exchangeable calcium and degree of calcium saturation; and (e) determination of readily soluble aluminum, iron, and manganese.

### DETERMINATION OF EXCHANGEABLE HYDROGEN IN SOILS

Of the exchangeable cations in soils, hydrogen is the most strongly adsorbed and consequently is the most difficult to replace by other cations. In clays having the 2:1 type lattice, exchangeable hydrogen is held largely by electrostatic or

ionic bonds. In the 1:1 lattice clays, in which there is little isomorphous substitution within the lattice, exchangeable H is bonded more strongly to the oxygen ions of the OH groups, although there is some question as to the position of the OH groups capable of dissociating into H ions (28). Hence, hydrogen-saturated clays of the 2:1 lattice type are more extensively dissociated and show much lower pH values than those of the 1:1 lattice group (34). Hydrogen clays of the 1:1 lattice group resemble more closely weak organic acids, and their dissociation is more markedly influenced by the pH of the suspension medium. For example, the amount of exchangeable hydrogen that can be replaced from soils containing predominantly 2:1 lattice clay by leaching the soil with  $N$   $\text{NH}_4\text{OAc}$  is quite independent of the pH of the  $\text{NH}_4\text{OAc}$  in the pH range 5 to 9, whereas in soils containing the 1:1 type clay it increases very markedly with the increasing pH of the replacing salt solution (57). When only a single (equilibrium) extraction with some salt solution is made, however, the amount replaced from soils containing either type of clay depends very much on the pH of the suspension medium at which equilibrium is established.

Moreover, the nature and the concentration of the salt solution used also influence the amount of exchangeable hydrogen that can be extracted from an acid soil, especially when only a single extraction is employed, which is the procedure followed in many of the rapid lime-requirement methods. As would be expected from the simple law of mass action, the amount of hydrogen replaced increases with increasing concentration of the salt solution and finally approaches a limiting value when the concentration of the salt reaches approximately 0.5  $N$ . Both the nature of the cation, that is, its charge and ionic radius, and the nature of the associated anion must also be considered in predicting the efficiency of a given salt solution in replacing exchangeable hydrogen. In the following four reactions,



the amount of hydrogen replaced from a constant amount of clay by the four salt solutions at equivalent concentrations will obviously be in the order (4) > (3) > (2) > (1). By far the greatest amount will be exchanged in reaction (4) owing to the formation of a weakly dissociated and volatile end product. Likewise because of the formation of weakly dissociated acetic acid, reaction (3) will proceed further than reaction (2). Indeed, it is for this reason that gypsum, even though more soluble than  $\text{CaCO}_3$ , will not correct soil acidity under field conditions. The slightly greater exchange of hydrogen in reaction (2), as compared with reaction (1), is due to stronger adsorption of the more highly charged calcium ion.

In the conductometric and potentiometric titrations of acid clays with strong bases, the influence of the nature of the cation in the added base is especially pronounced. Most hydrogen-saturated clays yield potentiometric titration curves that strongly resemble those shown by weak monobasic organic acids (7, 33, 34, 35). The monobasic character of the colloidal clay acid is undoubtedly due to the fact that the dissociation constants of the different exchangeable hydrogens on the colloidal particle do not differ sufficiently to permit detection by the potentiometric method. The potentiometric titration curves for clays, however, differ from those given by weak organic acids in two respects: first, the equivalence points are more indefinite because of the continued interaction of the clay with the added base, and second, the pH value for any given degree of neutralization varies with different cations in accordance with the well-known lyotropic series. With some clays, which tend to decompose at higher pH values with formation of soluble silicates and aluminates, the equivalence point must be chosen rather arbitrarily. In general, however, equivalent amounts of hydrogen are neutralized by different bases if the midpoint on the steepest part of the curve is chosen as the equivalence point.

The titration curve of a weak monobasic organic acid such as acetic acid is very accurately given by the following equation:

$$\text{pH} = \text{pK} + \log \frac{[\text{NaAc}]}{[\text{HAc}]} + \log \gamma_{\text{Ac}^-} \quad (5)$$

in which  $\text{pK}$  is the negative logarithm of the true (thermodynamic) dissociation constant;  $\gamma_{\text{Ac}^-}$  is the activity coefficient of the acetate ion and depends upon the ionic strength of the solution; and the brackets denote the concentrations of the salt and the undissociated acid. Obviously, the pH value at 50 per cent neutralization must be equal to the  $\text{pK}$  value of the acid in sufficiently dilute solutions, and indeed this is one of the methods employed for determining dissociation constants of weak organic and inorganic acids. Bradfield (7) has used the following approximate form of equation (5) to characterize the strength of clay acids:

$$\text{pH} = \text{pK} + \log \frac{[M\text{-clay}]}{[H\text{-clay}]} \quad (6)$$

in which  $M$  represents the cation of the added base;  $\text{pK}$  is the negative logarithm of the "apparent dissociation constant" of the clay acid; and the brackets denote milliequivalents of adsorbed cations per 100 gm. of clay. Jenny (26, p. 33) has objected to this simple analogy because the apparent  $\text{pK}$  value of the clay acid as obtained from the potentiometric titration curve depends upon the nature of the base employed. But it must be remembered that although the salts of weak organic acids are completely dissociated, the clay salts are only partly dissociated and behave as weak electrolytes, as recently shown by Marshall and Krinbill (34). In deriving this equation relating pH to degree of neutralization of the clay acid analogous to that for a weak monobasic organic acid it is neces-



sary, therefore, to substitute  $[M\text{-clay}] \alpha_M$  for  $[M\text{-clay}]$ , so that equation (6) becomes:

$$\text{pH} = \text{p}K + \log \frac{[M\text{-clay}]}{[H\text{-clay}]} + \log \alpha_M \quad (7)$$

where  $\alpha_M$  is the degree of dissociation of the cation of the added base adsorbed on the clay. It is tacitly assumed, of course, that the degree of dissociation of the exchangeable metal ion  $M$  is large as compared with that of exchangeable hydrogen. When this modified equation is used, the apparent  $\text{p}K$  value of the clay acid as obtained from the potentiometric titration curve becomes independent of the nature of the base employed. For a given degree of neutralization of the clay acid with different bases, the higher the degree of dissociation of the cation adsorbed on the clay, the higher will be the pH of the clay suspension. For cations having the same charge, the greater the hydration of the adsorbed cation, the greater will be its degree of dissociation, and consequently the higher will be the pH value of the clay suspension for equivalent amount of the base added. Likewise, clays neutralized with hydroxides of bivalent cations should be less completely dissociated and should have lower pH values than the same clays treated with equivalent amounts of hydroxides of monovalent cations. These observations have been verified by many investigators (7). Granting that this simple analogy between colloidal clay acids and soluble weak monobasic acids is not rigorous, nevertheless the authors find it very useful.

Thus the pH value of the clay suspension produced by addition of equivalent amounts of different bases usually varies in accordance with the well-known lyotropic series. Deviations from the lyotropic series noted in certain clays have been attributed to the difference in size of the cations in relation to the lattice configurations that give rise to cation exchange (18). At the equivalence point (midpoint on steepest part of the curve) the pH value of Ca-clay, for example, is about one unit lower than that of Na-clay, but equivalent amounts of NaOH and  $\text{Ca}(\text{OH})_2$  are usually taken up by the clay at the equivalence point. In determining exchangeable hydrogen by potentiometric titration, it is best, however, to use  $\text{Ca}(\text{OH})_2$  and to allow sufficient time for establishment of equilibrium, as the pH of the clay suspensions for any given amount of the base added decreases with time. This is usually done by adding increasing amounts of  $\text{Ca}(\text{OH})_2$  to a series of flasks containing the same amount of clay and allowing the suspensions to stand for several days before making pH measurements. The effect of time of reaction on the pH value of the soil suspension is very pronounced with soils of high organic matter content and must be fully considered in any rapid estimation of the lime requirement by potentiometric titration.

It is evident from equation (7) that, for the same degree of neutralization, the greater the apparent  $\text{p}K$  value of the clay acid, the higher will be the pH value of the clay. The pH value of the clay suspension at any point on the titration curve for a given base will therefore depend upon the nature of the clay. Hydrogen-saturated clays of the 2:1 lattice group, as already pointed out, are more extensively dissociated and therefore show lower pH values than clays of the 1:1

lattice type at equivalent degrees of neutralization. For this reason, some caution must be exercised in estimating the degree of base saturation of the soil from its pH value. This point has been emphasized by Mehlich (39).

Conductometric titration of an acid soil or clay with hydroxides of different cations gives widely different values for exchangeable hydrogen, none of which agree with the results of the potentiometric method. With some clays, however, the amount of exchangeable hydrogen obtained by conductometric titration using NaOH is in very good agreement with values given by the equivalence point on the potentiometric titration curve using either NaOH or  $\text{Ca}(\text{OH})_2$ . The amount of exchangeable hydrogen as determined by conductometric titration of H-clay with  $\text{Ca}(\text{OH})_2$  may be 50 per cent higher than that obtained with NaOH. The results with  $\text{Ba}(\text{OH})_2$  according to Hissink's method (21) may be even higher than those obtained with  $\text{Ca}(\text{OH})_2$ . Bradfield (6) has attributed this discrepancy between the results of conductometric titration with hydroxides of monovalent and bivalent cations largely to formation of the more insoluble and less dissociated aluminates and silicates of the bivalent cations. In addition to this difficulty, the results of a conductometric titration of an acid clay with a base when plotted in the usual manner seldom yield a pair of straight lines, characteristic of weak organic acids, that can be extrapolated accurately. Indeed, as Marshall and Krinbill (34) have shown, the conductometric titration curves of clays may be very complex and difficult to interpret. It is perhaps for this reason that the conductometric method for determining exchangeable hydrogen is now less commonly employed than the potentiometric method.

From the foregoing discussion it should be evident that the different methods for determining exchangeable hydrogen are empirical and give widely divergent results. The concept of exchangeable hydrogen is, of course, intimately involved in any definition of "base-saturated soil" and "cation-exchange capacity." Bradfield and Allison (8, 9) have proposed that a fully base-saturated soil be defined as one which has reached equilibrium with an excess of  $\text{CaCO}_3$  at the partial pressure of  $\text{CO}_2$  existing in the atmosphere and at a temperature of  $25^\circ \text{C}$ . Admittedly, this is the most logical definition for base-saturated soils existing in nature, and although the residual carbonate method described by Bradfield and Allison (8) is not well suited for routine work it should serve as a standard for comparison in the determination of exchangeable hydrogen as well as in the rapid estimation of the lime requirement of soils.

Among the methods involving extraction of exchangeable hydrogen by leaching the soil with some salt solution, the ammonium acetate method (13, 51, 61) is commonly employed largely because it is especially well suited for simultaneous determination of exchangeable metal ions and exchange capacity of soils. The advantages of normal ammonium acetate as a replacing salt solution have been pointed out by Schollenberger and Dreibels (61). The solution is well buffered at pH 7 and is therefore very effective in replacing adsorbed hydrogen. Because of the high concentration of ammonium ions, the amount of exchangeable hydrogen replaced by leaching the soil with neutral  $N \text{ NH}_4\text{OAc}$  solution corresponds more closely to that given by the potentiometric titration of the hydrogen-

saturated soil with  $\text{NH}_4\text{OH}$  to about pH 8.3, which represents approximately the equivalence point. As already indicated, values for exchangeable hydrogen, and consequently exchange capacity, of soils containing predominantly 2:1 lattice clay and of those containing 1:1 lattice clay are differently affected by the pH of the ammonium acetate solution (57). It should be mentioned also that, at least on soils containing clays of the 2:1 lattice group, the values given by the ammonium acetate method are in good agreement with those obtained by Bradfield and Allison's residual carbonate method (8, 12, 41); on organic soils, however, the ammonium acetate method gives low results as compared with methods employing bivalent cations (41).

There are, of course, important sources of error in the ammonium acetate method. The direct potentiometric titration of exchangeable hydrogen in the highly buffered ammonium acetate extracts using the glass electrode must be thoroughly standardized and carried out very carefully, otherwise an error of even 0.1 pH in the pH measurement may lead to appreciable errors. For this reason, the amount of exchangeable hydrogen in the ammonium acetate extract is often calculated by subtracting the sum of the exchangeable metal ions from the exchange capacity as determined by the ammonium adsorption method. All errors in the determination of individual exchangeable metal ions and exchange capacity will then fall on the determination of exchangeable hydrogen. As pointed out by Shaw (63) and Peech (51), the common practice of using an ammoniacal alcoholic wash solution in determining the amount of ammonium adsorbed by the soil is certain to lead to high results for exchange capacity and exchangeable hydrogen as calculated by difference.

Another promising method for determining exchangeable hydrogen, proposed by Mehlich (38), makes use of 0.5 *N*  $\text{BaCl}_2$  dissolved in an aqueous 0.2 *N* triethanolamine solution adjusted to pH 8.2 as the replacing solution. This reagent is exceptionally well buffered at this pH and is therefore very effective in replacing adsorbed hydrogen. Unfortunately, because of inherent analytical difficulties attendant in the determination of exchangeable calcium, magnesium, potassium, and sodium in the presence of large amounts of barium, this extracting solution is not so suitable as the ammonium acetate reagent for simultaneous determination of exchangeable metal ions.

#### RAPID DETERMINATION OF THE LIME REQUIREMENT OF SOILS

The term "lime requirement" is somewhat ambiguous and has been often used by different investigators to mean the amount of lime that must be applied to the soil to bring the soil reaction to neutrality or to some other desired pH value as determined by some specified method. Or, as the term is sometimes used, it is simply the amount of lime that must be applied to the soil to grow a certain crop. Nearly all proposed methods for rapid determination of the lime requirement of soils essentially involve determination of exchangeable hydrogen. Like the different methods for determining exchangeable hydrogen, the rapid lime-requirement methods give widely divergent results which have little meaning unless the method is clearly defined.

Among the methods involving use of hydroxides, that of Veitch (66) was very popular at one time. This method consists of titrating the soil with  $\text{Ca}(\text{OH})_2$  to the phenolphthalein end point and, as would be expected, gave high results. Sodium carbonate (10) has also been employed for this purpose, but inasmuch as the pH values produced by hydroxides of the alkali metals are considerably higher than those given by equivalent amounts of  $\text{Ca}(\text{OH})_2$ , such methods are more empirical. The better lime-requirement procedures today, involving use of hydroxides, are based on serial potentiometric titration of the soil with  $\text{Ca}(\text{OH})_2$  using the glass electrode. This is essentially the method described by Dunn (16). In the method proposed by Hardy and Lewis (19) the soil is titrated with  $\text{Ca}(\text{OH})_2$  to pH 7.0 in the presence of  $\text{CaCl}_2$  in order to hasten establishment of equilibrium. Although the equivalence point may not be changed appreciably by addition of salt, the pH values at any point on the titration curve are much lower in the presence of salt. This must be taken into consideration in estimating the amount of lime necessary to bring the soil in the field to the desired pH value.

The more rapid methods for assessing lime needs of soils are based on single extraction of exchangeable hydrogen with some salt solution and subsequent titration of the soil extract with a standard base solution. It has already been shown that use of salts of strong acids, such as  $\text{KNO}_3$  in the method described by Hopkins (66), does not give complete replacement of exchangeable hydrogen. Hence, such procedures invariably give low results. The method proposed by Jones (27), involving the use of  $\text{Ca}(\text{OAc})_2$ , is more satisfactory and was widely accepted by American investigators. But this method also tends to give low results on heavier acid soils because  $\text{Ca}(\text{OAc})_2$  solution is strongly buffered at too low a pH value to effect complete replacement of exchangeable hydrogen. The acetate buffers show maximum buffer capacity at pH 4.76 which, of course, is numerically equal to the  $\text{pK}$  value of acetic acid [compare equation (5)]. A more desirable extracting solution should be strongly buffered at pH 7 and obviously should contain the salt of a very weak acid having a  $\text{pK}$  value of approximately 7. A solution of *p*-nitrophenol ( $\text{pK} = 7.1$ ), partly neutralized with  $\text{Ca}(\text{OH})_2$ , meets this requirement admirably well and is the basis of Schofield's method (60). The method, however, gives lower results for exchangeable hydrogen than does Mehlich's method (38) or Bradfield and Allison's method (8) as shown by Innes and Birch (25).

The rapid method for routine determination of exchangeable hydrogen described by Bradfield and Allison (8) makes use of  $N \text{ NH}_4\text{Cl}$ - $0.01 N \text{ NH}_4\text{OH}$  solution for extraction. The solution has a pH value of 7.4 and is strongly buffered at this pH value. The results obtained are in good agreement with those obtained by the residual carbonate method, the ammonium acetate method, and the barium chloride-triethanolamine method (25, 41).

Brown (11) recently described a rapid method for determining lime requirement of soils based on a single extraction of the soil with neutral normal ammonium acetate and subsequent determination of the pH value of the extract by means of the glass electrode. From the change in pH value of the ammonium acetate solution, the amount of exchangeable hydrogen is obtained



directly from a calibration curve prepared by plotting the pH value of the ammonium acetate solution to which different amounts of acetic acid were added. Because the ammonium acetate solution is highly buffered at pH 7, changes in pH are small and must be measured very accurately. The method should be quite suitable for routine determination of the lime requirement of soils.

Of the more indirect lime-requirement methods, that proposed by Comber (14) was very popular at one time and is still used by some of the state soil-testing laboratories. In this method the soil is treated with an alcoholic solution of KCNS, and the intensity of the characteristic red color of the ferric thiocyanate complex serves as a measure of the soil acidity and the lime requirement of the soil. The method is much too empirical because other factors besides pH, such as oxidation-reduction status of the soil, organic matter content, and presence of iron complex forming ions, influence the solubility of iron in the soil.

Laboratory results obtained by a given lime-requirement method must be multiplied, of course, by an appropriate "liming factor" (16), which should take into account losses by leaching as well as by crop removal and especially the chemical composition and fineness of the limestone, in order to arrive at the amount of lime that must be thoroughly incorporated into the soil to bring the reaction to the desired pH value within a specified time under field conditions. Schollenberger and Salter (62) have published a very useful chart for evaluating the probable rate of reaction of any ground limestone applied at practical rates if the chemical composition and the particle-size distribution of the limestone are known.

#### DETERMINATION OF SOIL REACTION

Methods for determining soil reaction were reviewed recently by Reed and Cummings (58). Of the chemical methods for estimating lime needs of soils, the soil reaction test is by far the simplest and is most commonly employed by state soil-testing laboratories and by county agricultural agents. Use of the colorimetric method is now primarily confined to field test kits, some of which are capable of giving results that agree within 0.2 pH unit with those of the electrometric method (36). The glass electrode has largely supplanted other electrometric methods because of rapid advances in construction of sturdy glass electrodes and suitable vacuum-tube potentiometers. The high resistance of the glass electrode necessitates use of special equipment such as a vacuum-tube amplifier or an electrometer. Also because of the asymmetry of the glass membrane, the electrode must be calibrated frequently, preferably with two standard buffer solutions. The glass electrode has been found to give thoroughly reliable results on all soils with the possible exception of certain saline soils containing large amounts of sodium carbonate. Special glass electrodes that show negligibly small error in the presence of a high concentration of sodium salts even at pH values as high as 10 are now commercially available. The quinhydrone electrode is much simpler and requires no elaborate equipment but has been found to give erroneous results with soils containing  $\text{MnO}_2$  (44). Also, quinhydrone electrodes should not be used on soils with pH values higher than 8 because dissociation of



hydroquinone, which is a weak acid ( $K = 1.75 \times 10^{-10}$ ), then becomes appreciable, and in addition hydroquinone in an alkaline medium is oxidized slowly by atmospheric oxygen.

There has been little agreement among different investigators as to use of the proper soil:water ratio in preparation of the soil suspension for pH measurement (58). Since the introduction of the more rugged type of glass electrodes suitable for measuring the pH values of soils at very low moisture content, the trend has been toward use of higher soil-water ratios. Inasmuch as the pH value of soils invariably increases with increasing dilution of the soil with water, one may well question the practical significance of soil reaction measurements at such high dilutions as 5 to 10 parts of water to 1 part of soil. Davis (15), however, has correctly cautioned against pH measurements at soil-moisture contents below the moisture equivalent because of the possibility of certain errors due to poor contact between soil and glass electrode and to high soil resistance which may yield an extraneous electromotive force in the grid circuit with certain types of vacuum-tube potentiometers. After a thorough survey of the literature, Reed and Cummings (58) concluded that "the pH value is erratic and unreliable when determinations are made on soils with moisture contents at the moisture equivalent or below." But inasmuch as pH measurements at such low moisture contents as the moisture equivalent necessitate use of a special type of glass electrode, use of 1:1 soil-water ratio, which has been adopted in several states (52), would appear to offer a good compromise, at least for routine determination of the soil reaction.

Within the entire range of moisture content from the moisture equivalent to the soil-water ratio of 1:5, the effect of dilution is, of course, to increase the pH of the soil suspension regardless of the initial pH value of the soil. Upon further dilution of the 1:5 soil-water suspension the pH remains fairly constant. This phenomenon has been ascribed to increased hydrolysis of the adsorbed metal ions with increasing dilution. Some of our unpublished results on hydrolysis of K-clay would refute this simple explanation. In this study, K-clay suspensions (Miami colloidal clay) were ultrafiltered and the degree of hydrolysis of K-clay was calculated from the amounts of potassium found in the filtrates. The degree of hydrolysis of K-clay was found to be directly proportional to the square root of the volume of dilution; the OH-ion concentration of the clay suspensions, therefore, should have been inversely proportional to the square root of the volume of dilution. Actually the OH-ion concentration of the K-clay suspensions was found to increase with dilution. Thus the pH of the clay or soil suspension increases upon dilution much as does the pH of a buffer solution consisting of a mixture of weak organic acid and its salt in accordance with equation (5). The increase, upon dilution, in pH of an acetate buffer, for example, is due to increase in the activity coefficient of the acetate ion with decreasing ionic strength of the solution. Returning to the analogous relationship given by equation (7) for clays which may be regarded as weak electrolytes even when fully base-saturated, one may formally attribute the increase in pH of soils upon dilution to increased dissociation of exchangeable metal ions. This simple

explanation may appear inadequate in light of data reported by Marshall and his associates (33, 34) showing that the fraction of the total exchangeable cations on the clay that is active, as measured by the clay membrane electrode, may increase or decrease upon dilution, depending on the nature of the clay. But quite aside from the general applicability and validity of equation (7), it is reasonable to suppose that the pH of a suspension of clay saturated with some exchangeable metal ion,  $M$ , should be largely determined by the degree of hydrolysis, which in turn should depend upon the degree of dissociation of  $M$ -clay. Regarding the increase, upon dilution, in pH of a suspension of clay completely or partly saturated with H, the simplest explanation, as suggested by Bradfield (7), is that "a part of the hydrogen on the surface of the acid-clay particle is ionized and is far enough removed from the particle to act as an ordinary (free) hydrogen ion when brought in contact with the electrode, but these ions are restrained by electrostatic forces from moving farther than this distance." From thermodynamic considerations, as given by Overstreet (45), it can be shown that the chemical potential and hence the activity of the hydrogen ions must be greater in the micellar solution than in the intermicellar solution, so the pH of the clay suspension should obviously increase as the proportion of intermicellar liquid in direct contact with the electrode increases. Mattson and Wiklander (37) have proposed a more complete theory, based on the Donnan equilibrium principle, to explain the effect of dilution and the addition of neutral salts on the pH value of soil suspensions.

Addition of a neutral salt like KCl to a soil suspension decreases the pH just as addition of an indifferent neutral salt decreases the pH value of a buffer solution such as NaOAc + HOAc. The lowering of the pH value of the acetate buffer, in the presence of a neutral salt, however, can be readily predicted from the decrease in the activity coefficient of the acetate ion with increasing ionic strength of the solution in accordance with equation (5). In acid soils, the decrease in the pH value upon addition of a neutral salt may be simply attributed to exchange of the adsorbed hydrogen by the cation of the added salt. But inasmuch as this effect of salts is equally pronounced even in neutral and alkaline soils (30, 56), other factors, such as the nature of the cation of the added salt and its degree of dissociation and hydrolysis when adsorbed by the clay, and the effect of the high concentration of salt on the degree of dissociation or the activity coefficient of the adsorbed cations, must be considered. Marshall and Bergman (33) have shown that the activity of the adsorbed potassium on the clay is not affected by addition of KCl to the K-clay suspension. In this respect the clay salts behave as strong electrolytes; hence, it would be incorrect to attribute lowering of the pH value of K-clay suspension upon addition of KCl to decrease in the degree of dissociation of adsorbed potassium in accordance with equation (7). Yet, is not the lowering of the zeta potential of K-clay in the presence of KCl (26, p. 50) usually attributed to the repressive effect of KCl on dissociation of K-clay? Likewise, the increase in pH of a saline soil upon irrigation can be best explained by assuming that the degree of dissociation and consequently

the hydrolysis of adsorbed sodium are increased upon removal of neutral sodium salts.

Regardless of exact mechanism, the influence of neutral salts on the soil reaction should be recognized in pH measurements. Many European investigators prefer to measure the pH value of soils in *N* KCl suspensions. The pH value obtained by this method is said to be a better index of soil acidity because it is not affected by the presence of soluble salts in the soil and is less subject to periodic fluctuations (56). The pH value of many soils in *N* KCl suspension, however, may be as much as 2 pH units lower than that measured in aqueous suspension at the same dilution. The method has been used very little in the United States, as it does not appear to offer any real advantage over the aqueous suspension method. In any studies of the correlation of soil reaction with plant growth and soil microbiological activity, the pH of the soil at optimum field moisture content and at time of sampling is usually the object of the determination.

The pH values of many soils undergo periodic variation (58), being lowest during the hot and dry season and highest during the cool and rainy season. This seasonal variation in pH value may be due to many factors, such as variations in CO<sub>2</sub> content of the soil air, nitrification, and differential removal of ions by plants, but in many instances it appears to be closely associated with fluctuations in amounts of soluble salts such as sulfates and nitrates which accumulate during the dry periods and thus lower the pH value of the soil, but which are subject to leaching during the rainy season, when the pH returns to its maximum value. In soils containing an excess of CaCO<sub>3</sub>, the partial pressure of CO<sub>2</sub> of the soil air, which in turn depends upon microbiological activity, largely determines the soil reaction (9).

Aside from any direct ecological significance of the hydrogen-ion concentration of soils *per se*, especially in relation to need for liming, the pH value also serves as a measure of the approximate degree of base saturation or the degree of calcium saturation of the soil, inasmuch as calcium is the predominant exchangeable metal ion in normal soils. It should be obvious that the pH of the soil is determined essentially by the ratio of the sum of the exchangeable metal ions to the amount of exchangeable hydrogen, the amounts of all exchangeable cations being expressed in milliequivalents per 100 gm. of soil. When applied to soils containing several different kinds of exchangeable metal ions, equation (7) can be rewritten as follows:

$$\text{pH} = \text{pK} + \log \frac{\sum [M_{i\text{-clay}}] \alpha_{M_i}}{[\text{H-clay}]} \quad (8)$$

which is of little use because little is known regarding the degree of dissociation of the different exchangeable metal ions or the mutual effect of the adsorbed cations on the degree of their dissociation. But inasmuch as Ca constitutes about 85 per cent of the total exchangeable metal ions, the pH of the soil is largely determined by this cation. By assigning some weighted mean value for the

degree of dissociation of all the exchangeable metal ions, which we may represent by  $\alpha'_M$  but which should not differ much from  $\alpha_{Ca}$ , and assuming that the values for  $\alpha'_M$  and  $pK$  are reasonably constant for any group of similar soils, equation (8) can then be replaced by the following approximate but more useful form:

$$pH = \text{constant} + \log \frac{\sum [M_i\text{-clay}]}{[H\text{-clay}]} \quad (9)$$

in which the new constant =  $pK + \log \alpha'_M$ . Since by definition the sum of all the exchangeable cations expressed in milliequivalents per 100 gm. of soil is equal to the exchange capacity, equation (9) can be rewritten in the following form:

$$pH = \text{constant} + \log \frac{[\text{Exchange capacity} - \text{Exchangeable hydrogen}]}{[\text{Exchangeable hydrogen}]} \quad (10)$$

Once the constant in equation (10) has been evaluated, a curve showing the relationship between the pH of the soil and the degree of base saturation can be readily constructed (49) and may be used to great advantage when making liming recommendations based on soil reaction. Furthermore, if the exchange capacity of the soil is known, the exchangeable hydrogen or the lime requirement can be thus readily estimated from the pH value with a fair degree of accuracy. The exchange capacity, of course, can be roughly estimated from the clay and the organic matter content of the soil or from the amount of exchangeable calcium, which is usually determined in routine soil testing. In practice, it is best to construct a nomogram or a table relating the lime requirement of the soil to its pH value and any one or more of the following variables; exchange capacity, texture, organic matter, and exchangeable calcium.

The value of the constant in equation (10) should be higher for soils containing clays of the 1:1 lattice group than for soils containing clays of the 2:1 lattice type and, according to data presented by Mehlich (39), should assume some intermediate position for organic soils. Data reported by Wilson and Staker (67), however, would indicate that the value of the constant for peat soils is lower than that of mineral soils containing either type of clay. For similar soils within a given region, the relationship between pH and degree of base saturation, as given by equation (10), is sufficiently valid (10, 49, 67) to permit its use in estimating the lime requirement of soils from their pH values. But, as Mehlich (39) has correctly pointed out, a single curve relating pH of the soil to degree of base saturation can be of little value for this purpose when applied to soils containing widely different types of clay.

#### DETERMINATION OF READILY AVAILABLE CALCIUM SUPPLY OF SOILS

In the absence of free calcium carbonate and water-soluble salts, exchangeable calcium constitutes not only the immediate supply of readily available calcium in the soil but also a large porportion of the total reserve supply of this plant nutrient element, especially in heavy-textured soils. Thus simple determination

of exchangeable calcium should afford an accurate measure of the total supply of readily available calcium in acid soils. Among the different extracting solutions proposed for determination of exchangeable calcium, the normal ammonium acetate is now most commonly employed.

On the other hand, accurate determination of exchangeable calcium in soils containing free  $\text{CaCO}_3$  is attended with many difficulties owing to solubility of  $\text{CaCO}_3$  in the extracting solution. Because of the well-known solvent action of ammonium salts on calcium carbonate, aqueous and alcoholic solutions of alkali chlorides have been employed in preference to ammonium salt solutions for extracting exchangeable calcium from calcareous soils (13, 55). In Hissink's method (13, 55) the soil sample is leached with two successive liters of  $N$   $\text{NaCl}$  solution. The first liter is assumed to contain all the exchangeable calcium plus the same amount of dissolved  $\text{CaCO}_3$  that is found in the second liter. Thus the difference between the calcium content of the two successive extracts was taken as the amount of exchangeable calcium present in the soil. Chapman and Kelley (13) proposed the use of  $0.2 N$   $\text{KCl}$  solution in 63 per cent ethyl alcohol for determination of calcium in calcareous soils. In their method the soil sample is leached with two 400-ml. portions of alcoholic potassium chloride solution and the amount of calcium found in the second 400-ml. portion is subtracted from that in the first. Because of the slight solubility of  $\text{CaCO}_3$  in the alcoholic solution, this method is capable of giving fairly accurate results. But all attempts to correct for calcium carbonate dissolved in the extracting solution involve assumptions that may lead to appreciable errors. The correction in Hissink's or Chapman and Kelley's method presupposes that the soil contains sufficient  $\text{CaCO}_3$  in proper physical form to saturate equally the two portions of extract. The presence of other water-soluble calcium salts would obviously tend to make the results high. It has been found that approximately correct values for exchangeable calcium may be obtained by Hissink's method largely because of compensating errors (13). The error due to incomplete replacement of exchangeable calcium by the first liter is compensated for to some extent by the greater amount of  $\text{CaCO}_3$  dissolved by the first liter.

Likewise the correction for dissolved calcium carbonate, based on determination of the carbonate content of the soil before and after extraction, is no better if carbonates of both calcium and magnesium are present, because proper apportionment of the carbonate to calcium and magnesium is impossible. As a simple expedient, the authors prefer to compute exchangeable calcium in calcareous soils by subtracting the sum of the exchangeable metal ions, excluding calcium, found in the ammonium acetate extract, from the exchange capacity as determined by the ammonium acetate method. Obviously, results for exchangeable calcium and magnesium obtained by this method will be in error if carbonates of both calcium and magnesium are present. Incomplete replacement of adsorbed calcium by ammonium acetate in the presence of large amounts of calcium carbonate (13, 63) will lead to somewhat lower values for exchange capacity and exchangeable calcium as obtained by difference. Shaw (63),



therefore, recommends complete extraction of adsorbed cations and carbonates by decomposing the carbonates with boiling ammonium chloride solution prior to leaching the soil with ammonium acetate solution.

For evaluating calcium-supplying power, there appears to be little reason for attempting to determine accurately the exchangeable calcium content of a soil that is fully saturated with calcium and is known to contain an excess of  $\text{CaCO}_3$ . Indeed, such a soil is adequately defined once it has reached equilibrium with an excess of  $\text{CaCO}_3$ ; the Ca-ion concentration in the soil solution is then determined primarily by the partial pressure of  $\text{CO}_2$  in the soil air and is quite independent of exchangeable calcium content or exchange capacity of the soil (9). Whether calcium in the carbonate form that may be present in unsaturated soils should be included with exchangeable calcium when evaluating the calcium status of the soil, is an open question. Such a condition, however, may be of considerable significance in determining calcium-supplying power and certainly must be recognized in estimating lime requirement of soils based on the pH value and the exchangeable calcium content of the soil.

The degree of calcium saturation has been considered by many investigators as an important factor in determining the calcium-supplying power and the need for liming soils (1, 2, 3, 40, 53). This single-value characteristic of the soil involves, of course, determination of exchangeable calcium and exchange capacity. Inasmuch as calcium is the predominant exchangeable metal ion in normal soils, the degree of calcium saturation, as already shown, can be estimated approximately from the pH value.

In the rapid microchemical soil tests for calcium (42, 50) the soil is extracted with dilute acid and neutral or acidic salt solutions, and the amount of calcium in the extract is estimated turbidimetrically by precipitation of calcium as the oxalate or preferably as the stearate (50). The sources of error in the rapid turbidimetric determination have been fully discussed elsewhere (50). In the absence of free  $\text{CaCO}_3$  in the soil, the different extracting solutions give comparable results. The acidic extracting solutions, however, dissolve large amounts of  $\text{CaCO}_3$  and dolomite, which may be present in naturally calcareous soils or which may have been recently incorporated into the soil, and thus give apparently high results for exchangeable calcium and magnesium. Peech (48) found, for example, that dolomite must first undergo decomposition in acid sandy soils before it can be effective in controlling magnesium deficiency in citrus. Obviously, this source of error must be considered in interpreting the results of soil tests for calcium and magnesium when dealing with soils that are likely to contain calcium and magnesium carbonates.

Nearly all the rapid chemical soil tests for calcium involve single extraction of the soil with dilute acid or salt solution and thus give incomplete replacement of exchangeable calcium in heavy soils. The procedure described by Peech and English (50), for example, extracts approximately 85 per cent of the exchangeable calcium of acid soils having exchange capacity between 15 and 20 m.e. per 100 gm. of soil.

DETERMINATION OF READILY SOLUBLE ALUMINUM, IRON, AND  
MANGANESE IN SOILS

Rapid microchemical tests for readily soluble aluminum, iron, manganese are often made in routine examination of soils (20, 42, 50). A detailed description of the more common of these tests and a discussion of the inherent sources of analytical errors in them have been presented elsewhere (50). A more novel method for extracting readily soluble ferrous iron in soils proposed by Ignatieff (24) makes use of 3 per cent  $\text{AlCl}_3$  solution. More recently Hoffer (22) described a rapid microchemical test for ferrous and ferric ions as an aid in diagnosing oxygen deficiency in soils. Comber's (14) lime-requirement test is, of course, based on the presence of soluble iron in acid soils. The tests for soluble iron and, especially, aluminum have been claimed to be useful in liming recommendations (20, 29, 42). Unfortunately, little is known about the chemistry of these three elements in soils, especially concerning their behavior in acid soils. Present chemical methods for determining readily soluble (or exchangeable) aluminum, iron, and manganese in soils are, therefore, very empirical and cannot be properly evaluated.

Although it can be readily shown that acid soils yield appreciable amounts of titrable acidity as well as soluble iron and aluminum upon extraction with some neutral salt solution like  $\text{NaCl}$ , the exact mechanism by which iron and aluminum are brought into solution in the presence of the added salt is not clear and has been the subject of many studies (43, 46). Two rather obvious mechanisms have been suggested. One is that acid clays contain, in addition to exchangeable hydrogen, some exchangeable aluminum and iron which are simply exchanged for the cation of the salt in the extracting solution. The other view is that iron and aluminum are liberated from acid soils, upon extraction with neutral salt solution, by secondary reactions, that is, dissolution or decomposition of the clay and other soil minerals in the presence of strong acid formed by replacement of exchangeable hydrogen by the cation of the added salt. Critical examination of these two schools of thought is beyond the scope of the present discussion. Moreover, the problem has been thoroughly reviewed by Paver and Marshall (46) and more recently by Mukherjee (43). Regardless of the mechanism, the amount of iron and aluminum brought into solution upon extraction of the soil with a neutral salt solution is highly correlated with soil reaction. This is true even when the soil is extracted with such highly buffered acidic solutions as sodium acetate at pH 4.8. For example, the amount of aluminum thus extracted from mineral soils in accordance with the rapid microchemical test previously described (50) may vary from as little as 10 pounds per 2,000,000 pounds of soil for neutral soils to as much as 1,000 pounds for very acid soils despite the fact that the pH of the highly buffered acetate solution is virtually unchanged during the extraction process. This would indicate that the readily soluble aluminum extractable by the sodium acetate solution at pH 4.8 is definitely a function of the initial soil reaction and is not brought into solution through decomposition of the clay minerals during the extraction process.

Nor can it be attributed to the simple cation-exchange reaction between the adsorbed aluminum and the sodium ions of the extracting solution, because extractions of the same acid soils with neutral normal ammonium acetate solution yield insignificantly small amounts of readily soluble aluminum even though aluminum acetate is soluble and forms a stable complex in neutral normal ammonium acetate solution at ordinary room temperatures. Ferric iron behaves similarly to aluminum except that there is good evidence (5, 46) that it can function in acid soils as an exchangeable cation, probably as some complex ion,  $[\text{Fe}(\text{OH})_2 \cdot 4\text{H}_2\text{O}]^+$  or  $[\text{Fe}(\text{OH}) \cdot 5\text{H}_2\text{O}]^{++}$ . The solubility of iron is also markedly influenced by the oxidation-reduction status of the soil (24, 59) as well as by soil reaction.

Displaced soil solutions and aqueous extracts even of strongly acid soils show the presence of relatively small and variable amounts of soluble iron and aluminum (17, 53, 54). As may be expected, the concentration of aluminum in true solution depends not only upon soil reaction but upon other factors such as soil organic matter content and presence of complex-forming ions (54). Because of the difficulties attendant in accurate determination of the small amounts of aluminum and iron in aqueous extracts and soil solutions, the method is now seldom employed.

The solubility of manganese in soils is governed by soil reaction as well as by the oxidation-reduction status of the soil, which in turn depends upon soil aeration and the supply of readily oxidizable organic matter (47, 59). Thus in well-aerated mineral soils the amount of exchangeable or bivalent manganese depends primarily upon soil reaction. In neutral and alkaline soils, the bivalent manganese undergoes rapid atmospheric oxidation to form insoluble manganese dioxide and higher oxides of manganese, but more recent evidence indicates that oxidation of the bivalent manganese in soils over a rather wide range in pH values may be carried out by microorganisms (31, 32). The amount of manganese as determined by leaching the soil with neutral normal ammonium acetate, the procedure commonly employed in determining exchangeable cations, is highly correlated with soil reaction and apparently represents the amount of bivalent or exchangeable manganese initially present in the soil (55, 64). On the other hand, the amount of manganese extractable by the sodium acetate solution at pH 4.8 in accordance with the rapid microchemical test previously described (50) bears no relation to soil acidity and exceeds considerably the exchangeable manganese content as determined by the ammonium acetate method (50). This is apparently due to rapid reduction of manganese dioxide in the soil by organic matter during the process of extraction with the acetate buffer at pH 4.8, whereas the rate of reduction of manganese dioxide by soil organic matter in the presence of the ammonium acetate solution at pH 7 is negligibly slow. For this reason, the ammonium acetate method for determining exchangeable manganese should be more useful for diagnosing manganese toxicity in acid soils than the methods employing dilute acids or acid salt solutions for extraction. It should be obvious that further work on the behavior of aluminum, iron, and manganese in relation to soil acidity is sorely needed for proper evaluation of

present chemical methods for studying these three much-neglected elements in soils.

#### VALUE OF THE DIFFERENT CHEMICAL TESTS

Not until the causes of poor growth of plants on acid soils and the nature of the responses of crops to liming are thoroughly understood, will it be possible to evaluate properly the relative usefulness of the different chemical methods that have been proposed for estimating lime needs of soils. Undoubtedly, the yield responses of crops to application of lime on acid soils are complex and involve many contributing factors, such as calcium deficiency and the toxicity of hydrogen ions, aluminum, iron, and manganese, the relative significance of which probably varies with different crops and soils.

During the last two decades there has been a growing tendency on the part of many soil and plant scientists to attribute poor growth of plants on acid soils primarily to calcium deficiency presumably brought about by low exchangeable calcium content and/or low degree of calcium saturation. Some of the studies in this laboratory already published (17) and now in progress would indicate that the beneficial effect of liming acid soils is not simply due to the increased supply of calcium as a plant nutrient. On the contrary, poor growth of even such crops as alfalfa on acid mineral soils cannot be attributed to low calcium supply in the soil. This is not surprising, as many acid mineral soils that must be limed for optimum growth of legumes may contain several thousand pounds of exchangeable calcium per acre-6-inches of soil. It is perhaps for this reason that some investigators have emphasized degree of calcium saturation as an important factor determining the calcium-supplying power of the soil (2, 3, 40, 53). Truog (66) believes that calcium must be absorbed by legumes as the carbonate or bicarbonate in order to compensate for nitrogen taken from the air by symbiotic nitrogen fixation. It is true that the degree of hydrolysis of the adsorbed calcium and consequently the Ca-ion concentration in soil solution should increase with the increasing degree of calcium saturation. But conductometric and potentiometric titrations of acid clays with  $\text{Ca}(\text{OH})_2$  fail to reveal any marked increases in the Ca-ion concentration in solution until the clay is fully saturated with calcium and in equilibrium with an excess of  $\text{CaCO}_3$  (8, 9). Even more significant in this connection are the data of Marshall and Ayers (35) who have shown that the activity of the calcium ions in certain clay suspensions, as measured by the clay membrane electrode, remains remarkably constant with the increasing degree of calcium saturation. Yet with many crops, maximum yield responses are obtained by liming acid soils to give about 60 per cent calcium saturation. Also, the fact that soluble calcium salts like gypsum fail to improve growth of legumes and many other crops on acid soils (17) would refute the theory that crop responses to liming are primarily due to increased supply of calcium as a plant nutrient. Unfortunately, many investigations on the effect of degree of calcium saturation of the soil on plant growth were conducted without controlling such associated variables as pH, amount of exchangeable calcium, and possible toxicity of manganese, aluminum, and iron at low pH values, and therefore the



real significance of the degree of calcium saturation in relation to the liming problem remains to be investigated.

Thus the test for exchangeable calcium alone would appear to be of little value in predicting calcium deficiency or need for liming soils, except possibly when one is dealing with extremely light soils having an exchange capacity below 2 m.e. per 100 gm.

Although toxicity of aluminum and iron has long been recognized as the possible cause of poor growth of plants on acid soils (14, 23, 54), these two elements as well as manganese appear to have received relatively little consideration in more recent liming investigations. As shown by Fried and Peech (17), manganese not only is very toxic to such lime-responsive crops as alfalfa but its presence in excessive amounts in the soil solution appears to interfere with calcium uptake by the plants. Much of the earlier work on the cause of poor growth of plants in acid soils dealt with toxicity of aluminum and iron in nutrient solutions, and although the toxicity of these elements and the significance of the manganese-iron ratio (65) have been well established by studies with nutrient solutions, very little is known about the extent to which the presence of salt-extractable aluminum, iron, and manganese in acid soils, as determined by the methods in common use, can modify the growth responses of different crops to application of lime on acid soils. But even a cursory examination of the literature would indicate that the presence of these three elements in acid soils cannot be ignored in studies dealing with responses of crops to lime. Determination of exchangeable manganese by the neutral ammonium acetate method, as already indicated, should prove very useful in liming recommendations.

Despite numerous studies on the effect of hydrogen-ion concentration on plant growth, it is very difficult to evaluate the true ecological significance of soil reaction in the presence of other complicating and associated variables. The more careful studies (4) with nutrient solutions and sand cultures, however, have shown that many plant species can make normal growth at pH values as low as those encountered in most acid soils. But quite aside from ecological significance, the simple test for soil reaction affords the most useful single-value characteristic for estimating lime needs of soils. No single chemical test alone, however, will likely prove infallible as a guide in liming recommendations.

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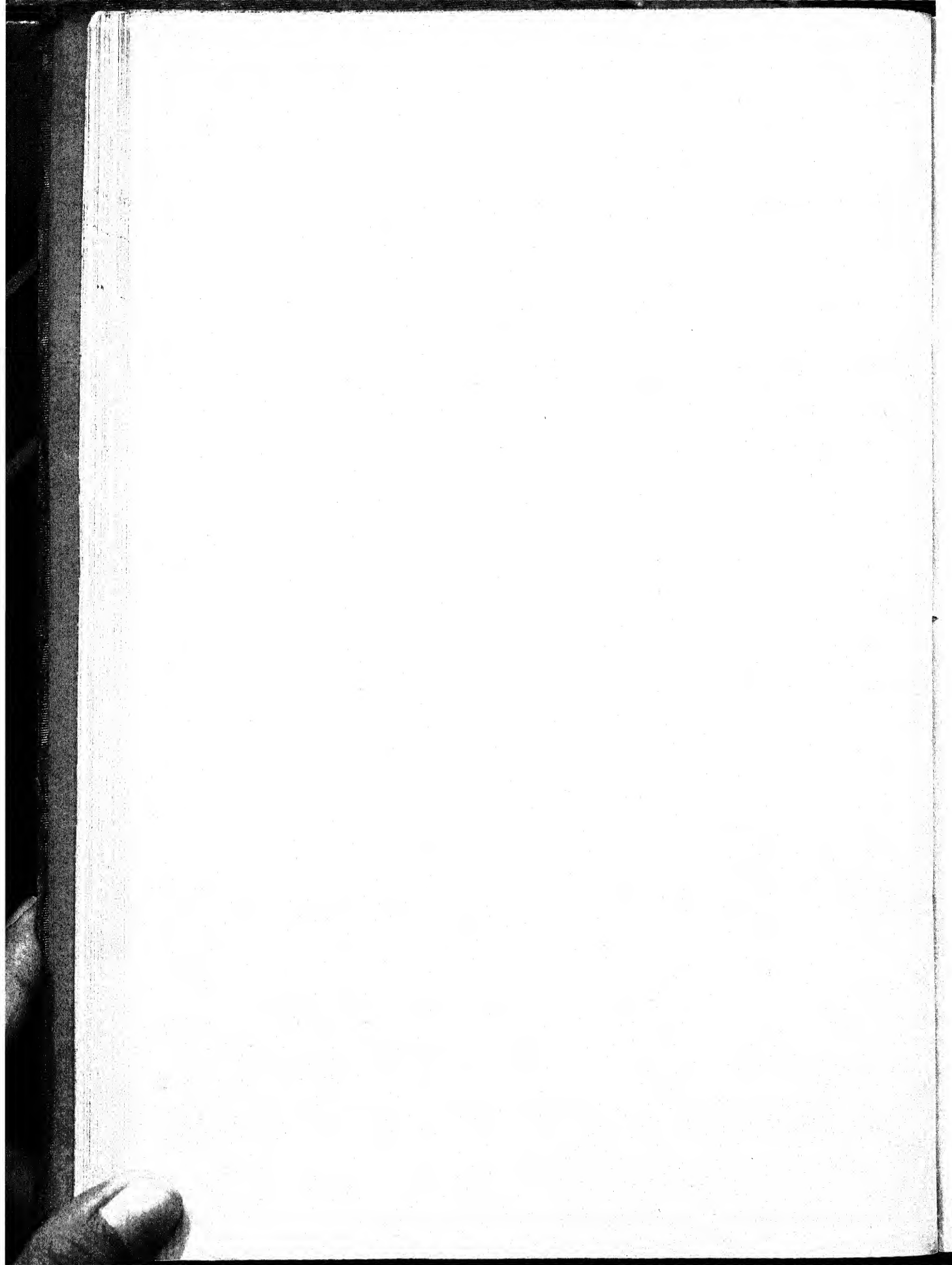
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## IONIZATION OF CALCIUM FROM SOIL COLLOIDS AND ITS BEARING ON SOIL-PLANT RELATIONSHIPS<sup>1</sup>

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Soil science, like every other science, advances broadly in two main ways: by the ever-widening generalizations of theory, and by technical improvements in methods of observation and measurement. Progress is especially rapid where these two factors interact favorably. Thus a new theory may stimulate more revealing measurements. Conversely, a sufficiently powerful new method of measurement may abruptly change the tenor of prevailing theory. The real measure of power of a new experimental weapon lies, not in greater novelty, precision, convenience, or rapidity, but in its immediate impact and cumulative bearing upon theory: to confirm, extend, modify, or overturn. In the long view, this is no less true of an applied than of a pure science. The most recondite theory of one generation not infrequently forms the basis of the "quick test" of the next. Soil scientists hardly need to be reminded of this. It has been mentioned because this discussion of the element calcium affords an opportunity to reexamine both our apparent and our hidden beliefs in the clear light of a new experimental method.

The whole concept of the cation-exchange mechanism of soils developed quantitatively as the result of two experimental procedures, one, analytical: the other, electrometric.

The analytical procedure represented the logical extension of the work of Thomas Way in an age of colloid-chemical enlightenment. The exchange relations of different cations were expressed by means of adsorption isotherms, and were, through the genius of Wiegner, related to the valency and hydration of the individual ions. Since these curves were simple and of the same general type, it became tacitly accepted that cations, and negatively charged surfaces also, differed in degree, but not in kind, in their manifestations of exchange reactions. As time went on, these conclusions were adopted as assumptions in the formal treatment of cation exchange. Thus Jenny (4) ascribed to each exchange ion of a given species upon a given surface a certain fixed oscillation volume, which was related to valency and ionic size, and therefore also to hydration. Cruder mass-action formulations of ionic exchange employed the same basic assumption that cations of the same kind were all alike, held by the same bonding energy and exchanging with the same degree of probability. Soil scientists should not forget, however, that it was from Wiegner's laboratory (17) and by analytical methods that striking exceptions were found in the exchange of calcium and ammonium. Ease of replacement was found, in certain cases, to depend very markedly upon the order in which the ions had originally been adsorbed by the surface.

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The second experimental weapon which greatly contributed to our knowledge of the relationship of ions to charged surfaces, and therefore aided in interpreting exchange properties of soils, was based upon development of the hydrogen electrode and formulation of the pH scale. Here the soil scientist felt himself to be on very secure ground. The soil could be treated in a formal way as a weak acid; the total acid content was identified with the total exchangeable hydrogen. The intensity factor was the readily measurable pH. No assumptions as to the identity of all the exchangeable hydrogen ions were needed. Examination of soil constituents by electrometric methods seemed, however, to emphasize the similarity between soil acids and soluble weak acids like acetic. The interpretation of humic acids by Odén (16) and of clay acids by Bradfield (2) followed this line. There seemed to be nothing in the pH titration curves of these soil constituents at variance with the view that all the hydrogen was essentially the same. If, then, the hydrogen ions were all alike, why should other cations show differences?

It is true that this conformist line of argument encountered difficulties. Thus titration curves of clay acids were manifestly different from those of soluble weak acids both at the extreme acid and the alkaline end of the range. At the acid end it was also evident that ionized aluminum was present; and in extremely alkaline solutions soluble silicates were formed. Over a broad range, however, the titration curves were unenlightening and left the observer with an uneasy suspicion that the acid groups were perhaps not all of the same strength; that some, certainly, were still being neutralized beyond the inflexion point of the pH titration curve. Yet even though the soil constituents might show complex properties as acids, there seemed, by analogy with the behavior of soluble acids and salts, no reason to expect wide differences in bonding energy for single metallic cations. Exchange reactions between soil constituents and salt solutions were therefore formulated as though all reactants were completely ionized. Certain observers, Mattson (15), Baver (1), and others more recently, obtained good evidence that the "clay salts" were not completely ionized. This was not particularly upsetting to contemporary ways of thinking, since although weak salts are unknown among soluble substances of low molecular weight, they seemed to fit particularly well into colloid-chemical concepts of the conditions of ionization in the electrical double layer. What was lacking was a direct measure of the ionization of soils and soil constituents for cations other than hydrogen. Soil scientists were acutely aware of this need. The cations of greatest interest, however, were calcium, magnesium, potassium, and sodium, all so strongly electropositive that metallic electrodes were out of the question for measurement of the small ionic activities that could be anticipated in soils.

There were two ways out of this difficulty. One was to investigate cations for which electrodes were available. Silver and thallium were studied by Marshall and Gupta (5). Serious limitations to their use were encountered, although in the case of silver it was clearly evident that only a small fraction of the exchange cations were ionized. The second alternative was to strive toward development of electrodes, or of membranes which would serve the same pur-

pose, by which the activities of the common exchange ions of soils could be determined. This avenue has been explored by the author and his associates since 1938. Membrane electrodes, formed, by a kind of poetic justice, of preheated clay films, have proved equal to the task of determining the single cations potassium (6), ammonium (9), sodium (10), calcium (12, 13), and magnesium (14) in the concentration range where they naturally fall in soil systems or in colloidal suspensions of soil constituents. Fairly complete studies of four important clay types—montmorillonite, beidellite, illite, and kaolinite—have been made with potassium (7), ammonium (8), sodium (10), and calcium (12). The procedure has been to obtain complete titration data for each clay at a variety of concentrations with each base. In such titration experiments the activities of both the metallic cation and the hydrogen ion are determined. In the case of sodium, the conclusions have been checked also by conductivity measurements.

To place that part of the work which deals with the element calcium in its proper perspective it is necessary to adopt some basis of comparison. The element sodium has been selected because calcium and sodium are, in soil science, widely regarded as the "normal" cations. Potassium is affected by fixation, although the effects are not apparent in simple titration experiments of the type considered, and magnesium forms a sparingly soluble hydroxide, and is suspected of existing in ionized form as  $\text{MgOH}^+$ ,  $\text{MgCl}^+$ , etc., as well as  $\text{Mg}^{++}$ .

#### SODIUM AND CALCIUM TITRATION CURVES

The pH, pNa, and pCa titration curves for Putnam clay, (fraction  $< 200 \text{ m}\mu$ , mineralogically a beidellite) are compared in figure 1. The fact that the concentrations of clay are not identical for the NaOH and  $\text{Ca}(\text{OH})_2$  titrations is not important to this discussion, which is concerned with the shapes of the curves rather than with their positions. The sodium pH curve shows more abrupt changes of slope than the corresponding calcium curve. In neither case would it be possible to anticipate any particular complexities as regards the meaning of the titration itself.

The pNa and pCa curves in the lower part of the same figure are spaced widely, and actually would be a little farther apart if the clay concentrations had been equal. This reflects chiefly the vast difference in the fraction active or ionized. The two curves both show changes of slope. The logarithmic scale, however, is not well suited to a detailed study, since the total range of pCa or pNa is small compared with that of the pH curves. A better comparison is afforded by figure 2, in which the measured activity of the sodium or calcium ion is plotted against the amount of base added. The calcium scale is multiplied by 10 so that the slope changes in the two cases will be more nearly comparable. The broken lines to the left give the calculated activities for complete ionization. The ratio of the slope of the experimental curve to this calculated slope gives the fraction active or ionized. We can thus readily analyze the significance of different parts of the curves in terms of the ionization of the particular cation employed.

The first features which attract attention are the changes in slope. In the

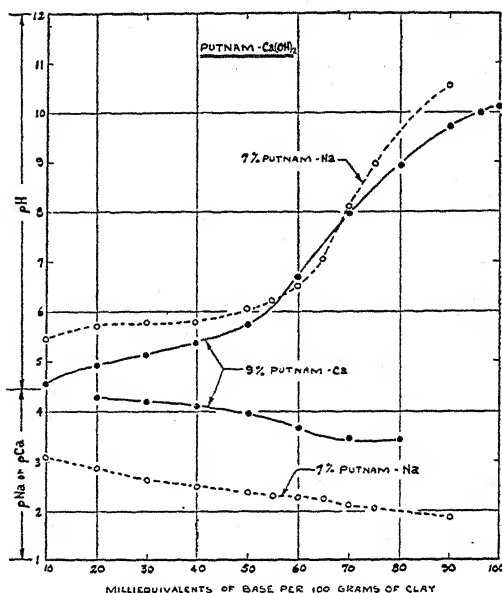


FIG. 1. pH, pNa, and pCa TITRATION CURVES FOR PUTNAM CLAY  
Sodium data by C. A. Krinbill; calcium data by A. D. Ayers

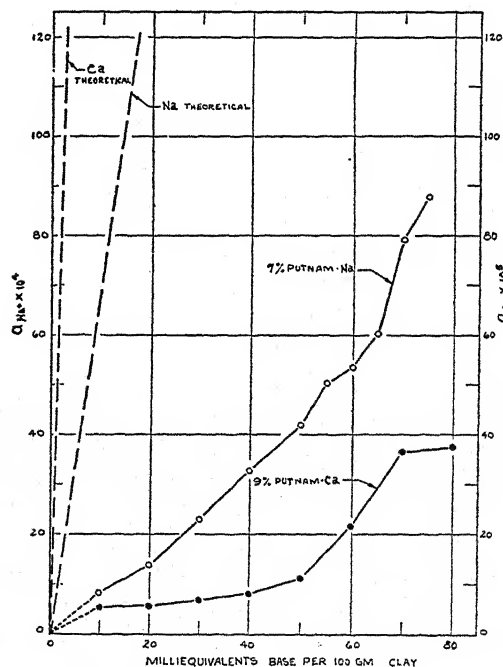


FIG. 2. RELATION OF ACTIVITIES OF SODIUM AND CALCIUM IONS TO AMOUNTS  
OF BASE ADDED TO PUTNAM CLAY  
Sodium data by C. A. Krinbill; calcium data by A. D. Ayers

sodium Putnam curve these may appear minor at the first glance; but even the smaller variations are real. They show themselves in the same places with different concentrations of clay, they are present also in the conductivity curves, and they are found at similar degrees of saturation with montmorillonite, which belongs to the same clay group. The short region from 55 to 60 m.e. has the smallest slope of any part of the curve and corresponds to a zone in which sodium is taken up with very much reduced ionization. In the case of montmorillonite, this is very marked indeed (fig. 3).

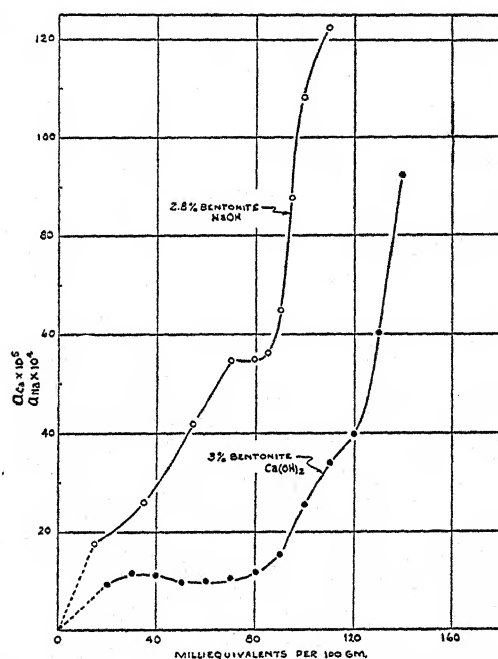


FIG. 3. RELATION OF ACTIVITIES OF SODIUM AND CALCIUM IONS TO AMOUNTS OF BASE ADDED TO BENTONITE

Sodium data by C. A. Krinbill; calcium data by A. D. Ayers

The corresponding calcium curve has a distinctly different character. For a considerable range of additions of base the slope is extremely small, then, at about 50 m.e. there is a marked increase which extends up to the point of equivalence. The calcium curve for montmorillonite shows exactly the same features, but even more strikingly, and from around 30 to 80 per cent neutralization with calcium hydroxide the calcium activity remains virtually constant. Calcium added over this broad zone is un-ionized to any measurable extent as may clearly be seen in figure 3.

The numerical differences in the active fraction which arise over the course of such titrations can best be appreciated by a tabulation of the values calculated for different parts of the titration curves. Some typical values are assembled in table 1. For sodium on Putnam clay they range from about 0.08 to 0.50; for calcium from 0.003 to 0.03. Bentonite gives a wider range in both cases.

## DIFFERENCES IN ENERGY OF ADSORPTION

Before discussing the corresponding figures for other clay minerals, let us consider what these differences for a given cation on a given clay mean. The measurement of cationic activity involves the mean electrochemical work which must be done in moving 1 mole from an infinite amount of the system under study to an infinite amount of a standard (molal) solution. The data are

TABLE 1  
*Fraction active for sodium and calcium over successive ranges of neutralization of the acid clay with base\**

CLAY	CONCENTRATION	NEUTRALIZA- TION CAPACITY TO INFLEXION	SODIUM		CALCIUM	
			Neutralli- zation	Fraction Active	Neutralli- zation	Fraction Active
		<i>m.e./100 gm.</i>	<i>per cent</i>		<i>per cent</i>	
Putnam < 200 m $\mu$ (beidellite)	7% (Na) 9% (Ca)	70	0- 14	0.121		
			14- 29	0.076	0- 29	.006
			29- 43	0.125	29- 43	.003
			43- 57	0.139	43- 57	.003
			57- 71	0.124	57- 71	.006
			71- 79	0.240	71- 86	.022
			79- 86	0.084	86-100	.029
			86- 93	0.189		
			93-100	0.514		
Bentonite < 200 m $\mu$ (montmorillonite)	2.8% (Na) 3.0% (Ca)	100	0- 15	0.412	0- 20	.031
			15- 35	0.142	20- 70	<.001
			35- 55	0.284	70- 80	.006
			55- 70	0.298	80- 90	.019
			70- 80	0.007	90-100	.066
			80- 85	0.114		
			85-100	1.20		
Kaolinite < 2 $\mu$	10%	3.0	0- 33	0.50	0- 39	.043
			33- 50	0.10	39- 59	.049
			50- 67	0.32	59- 79	.156
			67- 83	0.18	79- 99	.195
			83-100	0.67		

\* Calculated from data by C. A. Krinbill, A. D. Ayers, and C. E. Marshall.

thermochemical, although the measurements are electrical and their interpretation in terms of activities is osmotic. If the addition of  $dn$  milliequivalents of base over part of the titration curve increases the activity of the cation by  $\Delta a_1$ , and over another part by  $\Delta a_2$ , then there must be a difference in the energy of adsorption amounting to  $RT \log \frac{\Delta a_1}{\Delta a_2}$ . Thus if  $\Delta a_1/\Delta a_2$  has a value 10 this difference amounts to about 1,400 calories per mole of the ion concerned. From the figures quoted above, the energy of adsorption of sodium on Putnam clay varies



over a range of about 1,100 calories per mole Na, and that of calcium over a range of about 1,400 calories per mole Ca, or 700 calories per equivalent. These calculations do not enable one to determine the total energies of adsorption; they involve differences only. These differences, however, are very appreciable. As a matter of fact they approach and may even exceed in order of magnitude the differences in energies of adsorption for different cations. Furthermore, the variations may be rather abrupt, the best example of this being the hydrogen bentonite-sodium hydroxide system (fig. 3) with its narrow zone, around 75 per cent neutralization, in which sodium having a very minute active fraction is taken up. Calcium shows a rapid change from the broad zone in which it has a very low active fraction to the zone of steady increase which starts just before the point of equivalence.

Certainly in the case of the two swelling-type clays of the montmorillonite group mentioned above, great differences in the energy of adsorption are found for the same cation. The ease of entry or of exit by exchange must also be strongly variable. The fact that relatively few exchange experiments have shown this, merely indicates that these are very insensitive in their usual integral form. Before any attempt is made to relate these facts to our knowledge of clay structure, it will be best to consider similar data for kaolinite, a clay which is different in structure from the montmorillonite group and ionizes by a different mechanism on the outer surfaces, probably at the crystal edges only.

#### COMPARISON OF KAOLINITE WITH SWELLING CLAYS

The figures quoted for the fractions active over different parts of the titration curve (table 1), and the corresponding changes in slope in the sodium and calcium activity curves (fig. 4) show that although kaolinite displays an increase in the fraction active with successive increments of base, there are no striking qualitative differences between Na and Ca such as were present in the montmorillonite clays. Kaolinite can be compared qualitatively with a weak acid having a series of dissociation constants of diminishing magnitude (Pauli's concept of colloidal acids in general). Its behavior approaches that of a soluble weak acid in several respects. The salts, both of Na and of Ca, are much more highly ionized than for montmorillonite, beidellite and illite, and they differ less from each other. When pH curves are drawn for the titration of different concentrations of kaolinite with sodium hydroxide they lie close together, being nearer in character to those of soluble acids,<sup>2</sup> whereas the montmorillonite clays give widely spaced curves reminiscent of strong acids.

Thus between the kaolinitic and montmorillonitic colloids there are very marked qualitative as well as quantitative differences in electrochemical behavior. These can be traced to the different atomic structures, and a consistent explanation based on these, though somewhat speculative at present, may briefly be considered.

<sup>2</sup> Over the range where the equation  $\text{pH} = \text{pK} \log \frac{\text{salt}}{\text{acid}}$  applies, soluble weak acids of different concentrations each give a single pH curve.

Starting with what we call a "hydrogen montmorillonite," which is actually a hydrogen-aluminum system, the first additions of sodium hydroxide cause chiefly a replacement of the H or Al ions external to the particles. The sodium activity is fairly high, since the ionic atmosphere is here expanding greatly in thickness because of the greater hydration of sodium as compared with H-Al. This process is very soon overshadowed by entry of sodium into the spaces between the lattice units. As is known from mechanical analyses, x-ray and electron microscope data, this entry of sodium tends to disperse the system. The distribution of c-axis spacings becomes less regular, and some surfaces which

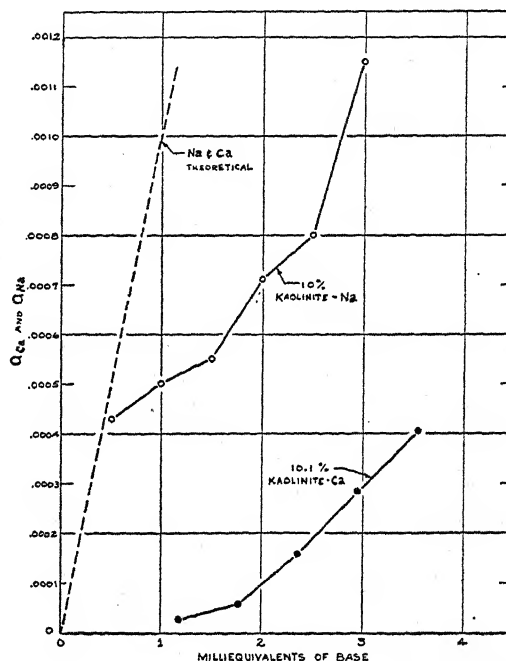


FIG. 4. RELATION OF ACTIVITIES OF SODIUM AND CALCIUM IONS TO AMOUNTS OF BASE ADDED TO KAOLINITE

originally were internal now become external. The measured activity of the sodium increases steadily, although the fraction that is active is less than in the first stage. Around 70 per cent neutralization the filling of the ionic atmosphere with sodium and the dispersive effect have temporarily reached an optimum. Additional sodium now enters internally only, and is taken up with little ionization. At about 85 per cent neutralization the process is completed, and further additions of base now serve to increase the effective charge and the ionization at the same time.

The case of calcium is simpler than that of sodium for two reasons: first, the character of the ionic atmosphere is changed much less; second, the c-axis spacings are particularly regular for Ca. In consequence, calcium, after an initial replacement of external H-Al, enters internally with little ionization over a

broad range. The final increase near the point of equivalence corresponds to the neutralization of more weakly acidic groups, perhaps those present at the plate edges.

Thus in both cases we can envisage a distinction between the electrochemical status of an ion taken up internally and that of one entirely external to the colloidal micelle. This is an important point, since from the pH measurements of Hauser and Reed (3) on H-montmorillonite fractions of different particle sizes it appears that no such conclusion can be drawn. The pH results, however, are probably rendered very insensitive to such effects by the presence of ionized aluminum in quantity.

The kaolinite curves, both for sodium and calcium, show no evidence of internal uptake. The ionic atmosphere dominates entirely. First the most exposed hydrogen ions are replaced; then hydrogen with less and less tendency to ionize is brought into reaction. The peculiar character of all the clays so far examined is that those groups which are the last to react with bases, that is, apparently the most weakly acidic, are the ones whose salts are most extensively ionized. The effect is something other than an ordinary hydrolysis, since it is easy to show from the pH measurements that hydroxyl ions equivalent to additions of base beyond the inflection point do not remain as such in the system. Whether they react entirely with the preexisting hydrogen ions of weakly acidic groups, or are adsorbed on the silicate surfaces, cannot be decided from this evidence alone.

#### FACTORS OF AGRONOMIC IMPORTANCE

We can now see that there are two great electrochemical differences between kaolinite and the montmorillonite clays which are likely to prove of agronomic importance. As table 1 shows, the exchange cations of kaolinite are more extensively ionized than those of the montmorillonite clays. This tends to compensate in some measure for their lower exchange capacity. The disparity is very great for calcium. Kaolinite does not show a broad zone where calcium is taken up with very minute ionization, as do the montmorillonite clays.

Because ionization of calcium is always less than that of monovalent ions like sodium and potassium, the ratio fraction-of-sodium-active: fraction-of-calcium-active for all clays is greater than the ratio exchangeable-sodium: exchangeable-calcium. Whereas the factor might range around 2-5 for kaolinite, it would lie between 10 and 50 for the montmorillonite clays. Thus the cationic environment of the plant root in a mixed system of monovalent and divalent ions will be entirely different in a soil electrochemically dominated by kaolinite from that in a soil similarly dominated by montmorillonite clays. One can see also, and this is especially true of calcium, that the ease of exchange against hydrogen will decrease more rapidly with successive removals for montmorillonite clays than for kaolinite clays. Below 70 per cent saturation with calcium the montmorillonite clays are characterized by an extremely low active fraction and hence by a high energy of adsorption for the Ca ion. They will exchange this calcium for hydrogen much less readily than they will the calcium which corresponds to higher degrees of saturation, say from 70-100 per cent.

To express the matter in terms of liming practice, the additions needed to bring the saturation up to 70 per cent, in the case of the montmorillonite clays, would make very little difference as regards improving conditions for uptake by growing plants. Somewhat more calcium is available for exchange, but it is held as firmly as ever. It can participate in movement by contact exchange probably only to a reduced extent. Above 70 per cent saturation with calcium the ionic environment of the plant root will contain more calcium, its movement by contact exchange will be easier, and its exchange against hydrogen ions from carbonic or other acids will be greatly facilitated. In the case of kaolinite, there is no region where calcium is so tightly held, and although additions at higher degrees of saturation are more effective than at low ones the transition is gradual. Hence on kaolinitic soils the relatively small amount of lime necessary to react with half the exchangeable hydrogen may show a good crop response. On a montmorillonitic soil the much larger quantity needed for the same chemical purpose would change the ionic environment of the plant root much less, and the response would presumably be poorer. Of course, in practice, the distinctions are not so clear-cut. Most soils contain organic matter, which contributes calcium in two ways: it holds exchangeable calcium, and it releases this on decomposition. So far there is no information on ionization of calcium from soil humic matter. We hope to obtain this as our work progresses. In attempting to correlate field response with the laboratory behavior of simplified systems, we must also consider the slow pace of reaction between ordinary ground limestone and exchangeable hydrogen of natural soils.

Of great importance also in soil-plant relationships are the effective ratios of different nutrient ions to one another, as well as their absolute amounts. Attention has frequently been drawn to the calcium:potassium ratio of the soil as a very crucial factor in controlling plant composition. Since potassium and sodium behave closely alike so far as activity measurements on clay suspensions are concerned, we may apply the evidence of table 1 in drawing some conclusions both on calcium:potassium and calcium:sodium ratios. It is immediately apparent that if soils dominated by montmorillonite and kaolinite respectively possess the same potassium:calcium or sodium:calcium ratio, then the ionic environment of the plant root as it encounters fresh exchange material will be entirely different in the two cases. In terms of ionized material the montmorillonitic soil will have by far the greater  $K^+ : Ca^{++}$  or  $Na^+ : Ca^{++}$  ratio. Secondly, if two such different soils were to contain the same amounts of exchangeable calcium, then the kaolinitic soil would provide a much richer source of ionized calcium than the montmorillonitic soil. This would be true also of potassium or sodium, but to a less extreme degree.

The situation in actual practice is not static. In the neighborhood of the active plant root we have both loss of cations to the root and renewal of the supply by contact exchange etc., from more remote regions. Regarding these rate processes we have little quantitative information. We can see qualitatively that there is a strong tendency to maintain the *status quo*. Thus local reduction of the exchangeable calcium below 70 per cent saturation for a montmorillonite soil

will cause a rapid decrease in the rate of removal, since from 70-30 per cent saturation the calcium is held with very great energy of adsorption. This same factor, however, will tend to increase the rate of renewal from adjacent undepleted parts by contact exchange.

There is yet another variable in plant growth in the field which affects the absolute levels of cationic activities and probably also their ratios to one another. This is soil moisture. Here much work lies ahead before definite pronouncements can be made. The new electrodes, however, can be used over almost as wide a range of moisture contents as the glass electrode. Field moisture conditions can therefore be investigated up to moderate pF values, thus entering the range where agricultural crops obtain the greater part of their nutrient supply.

Electrometric study of nutrient cations present in soils promises, therefore, not merely improvement in our theoretical approach but a very practical interpretation of much that has remained mysterious in field experiments. Calcium will naturally receive consideration, not merely because it is the most abundant exchange cation and the most widely used ameliorant, but especially for its crucial role in determining the balance of composition of the growing plant.

#### SUMMARY AND CONCLUSIONS

The following conclusions are drawn from an examination of the complete titration curves (including electrometric  $\text{Na}^+$  or  $\text{Ca}^{++}$  determinations) of Putnam clay (beidellite), Wyoming bentonite (montmorillonite), and kaolinite with sodium and calcium hydroxides:

In the montmorillonite and beidellite clays the fraction that is active varies abruptly for sodium and for calcium at different stages of neutralization. Sodium shows a narrow zone and calcium a broad zone of very low activity. Kaolinite shows a fairly steady rise in fraction active for both cations as the amount of base is increased.

These differences in active fraction reflect large differences in differential heat of adsorption of the cation in different regions of the titration curves. Exchange ions of a given kind are thus held with a wide range of bonding energies.

Kaolinite shows great electrochemical differences from the montmorillonite clays. Ionization of all cations, but especially of calcium, is much greater for kaolinite than for the montmorillonite clays.

The bearing of these results on the interpretation of practical field experience is discussed.

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## INFLUENCE OF CALCIUM ON AVAILABILITY OF OTHER SOIL CATIONS<sup>1</sup>

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Investigation of the nutrient-cation status and needs of 20 of New Jersey's most important agricultural soils led to publication of the following tentative statement (1):

For the ideal soil, it is suggested that 65 per cent of the exchange complex should be occupied by Ca, 10 per cent by Mg, 5 per cent by K, and 20 per cent by H.

This statement emphasizes the importance of Ca *per se*. It also infers that consideration must be given to the ratios between the amounts of the several exchange cations. Thus it suggests a Ca-Mg ratio<sup>2</sup> of 6.5:1, a Ca-K ratio of 13:1, a Ca-H ratio of 3.25:1, and a Mg-K ratio of 2:1. If a total exchange capacity of 10 m.e. is assumed, the plow depth of such a soil would contain about 2,600 pounds exchange Ca, 243 pounds exchange Mg, and 390 pounds exchange K.

Data from which the foregoing conclusion was reached were obtained in a series of studies that have been under way since 1940. Some of the results of these studies have been published. The purpose of this paper is to bring the findings up to date.

The first study was designed to determine what constituted an optimum Ca-K ratio for alfalfa when grown on Dutchess shale loam. In preparation for this work the exchangeable bases were removed from the soil and then restored in accordance with a definite plan. This called for uniform amounts of exchange H and Mg and variable amounts of exchange Ca and K. Hardistan alfalfa was then planted and grown through seven successive harvests.

It was found in this study (5) that the alfalfa plant could adjust itself to very wide Ca-K ratios in the soil, making good growth at ratios anywhere between 100:1 and 1:1. Ratios within the plant, however, were much narrower than those in the soil. With a Ca-K ratio of 32:1 in the soil the Ca-K ratio in the plant was only a little over 3:1. Thus the rate of absorption of K by the plant was 10 times that of Ca. Without further additions of Ca or K to the soil, the Ca-K ratios in the successive harvests increased to 3.9, 4.3, 7.4, 9.1, 10.0, and 11.1:1.

As soon as the Ca-K ratio in the alfalfa rose above 4:1 the yields dropped off, but K-deficiency symptoms were not apparent until the Ca-K ratio had risen to approximately 8:1. A Ca-K ratio of 4:1 in such alfalfa corresponded to a Ca content of about 2 per cent and a K content of about 1 per cent. Thus the con-

<sup>1</sup> Paper of the Journal Series, New Jersey Agricultural Experiment Station, Rutgers University, department of soils.

<sup>2</sup> All the ratios mentioned in this paper are cation-equivalent ratios.

clusion was reached that the K content of alfalfa should not be allowed to fall below 1 per cent. This, therefore, was set as the critical level for this element in alfalfa. To date, not a single sample of K-deficient alfalfa, as evidenced by white spots around the edges of the leaves, has been found to contain more than 1 per cent K.

TABLE 1  
*Exchange-cation status and Ca-K and Ca-Mg ratios in original soils  
in comparison with "ideal" soil*

SOIL TYPE	pH	CATION- EXCHANGE CAPACITY	PERCENTAGE SATURATION OF COMPLEX WITH				Ca:K	Ca:Mg
			H*	Ca	Mg	K		
		<i>m.e.†</i>						
Dutchess shale loam.....	7.2	14.8	0	103.3	23.6	4.7	21.8	4.4
Collington loam.....	4.7	15.9	60.6	28.3	8.1	3.0	9.3	3.4
Penn silt loam.....	4.5	19.8	88.0	2.0	8.0	2.0	1.0	0.2
Washington loam.....	4.6	11.3	67.7	14.1	16.8	1.4	9.5	0.8
Hoosic loam.....	6.9	11.4	18.3	71.0	8.7	1.2	57.4	8.1
Sassafras loam.....	4.5	7.5	86.4	5.3	5.3	3.0	1.7	1.0
Dover loam.....	7.3‡	14.0	0.0	68.5	25.0	1.5	43.2	2.7
Bermudian silt loam.....	6.1	13.2	24.6	48.4	25.7	1.3	35.5	1.9
Colts Neck sandy loam....	4.2	9.9	92.2	2.0	3.0	1.2	2.4	0.7
Lansdale silt loam.....	4.6	13.0	60.8	25.0	11.5	2.7	9.2	2.2
Chester loam.....	5.8	10.6	75.0	14.1	9.3	1.6	8.6	1.4
Merrimac silt loam.....	4.4	10.2	81.1	2.9	14.7	1.3	0.2	0.0
Fox gravelly loam.....	7.4‡	8.5	0.0	71.7	40.7	2.0	34.8	1.9
Gloucester loam.....	5.4	11.9	79.8	14.2	5.0	1.0	14.8	2.8
Hagerstown loam.....	7.7‡	16.5	0.0	78.1	25.4	1.3	58.9	3.1
Whippany silty clay loam..	5.2	8.7	44.5	36.7	17.2	1.6	22.2	2.1
Sassafras loamy sand.....	4.4	2.7	99.3	0.2	0.0	0.5	0.2	0.0
Sassafras sand.....	3.9	2.0	99.4	0.5	0.0	0.1	10.0	0.0
Papakating stony loam....	5.6	9.0	44.3	44.4	7.7	3.6	12.1	5.8
Lakewood sand.....	4.4	2.8	93.7	3.0	3.0	0.3	11.7	1.0
"Ideal" soil.....	6.5	10.0	20.0	65.0	10.0	5.0	13.0	6.5

† Per 100 gm. soil.

\* By difference.

‡ Free Ca- and Mg-carbonates present.

A second study (2) had to do with the application of these findings to 20 of the most important agricultural soils of New Jersey. Samples of the A-horizons of mostly virgin soils<sup>3</sup> were collected for this work and subjected to laboratory analysis. The data (table 1) reveal that not one of these soils contained exchange cations in ratios that even approached those of the suggested ideal soil. Thus the calcareous soils of the Dutchess, Dover, Fox, and Hagerstown series appeared to contain no exchange H, whereas the soils of the Penn, Colts Neck, Sassafras,

<sup>3</sup> The Dutchess, Hoosic, Hagerstown, and Fox soils were chosen from areas that had been under cultivation.

and Lakewood series contained exceedingly high percentages of it. All 20 soils showed a need for K, 15 of them for Ca, 11 for Mg, and 5 for H, if the exchange cation specifications for the ideal soil were to be met.

In preparing these soils for greenhouse studies it was decided to apply dolomitic limestone to pH 6.5, supply a liberal and uniform quantity of superphosphate, and add small amounts of the essential minor elements. K was then added as

TABLE 2  
*Ca-Mg and Ca-K ratios in limed\* and phosphated soils, yield of alfalfa on these soils with and without added K, and harvest at which K became < 1 per cent*

SOIL SERIES†	Ca:Mg IN SOIL AT START	Ca:K IN SOIL AT START		DRY MATTER PER POT		NUMBER OF HARVEST WHEN K CONTENT BECAME < 1 PER CENT	
		No K	200 K	No K	200 K	No K	200 K
				gm.	gm.		
Dutchess.....	4.5	22	17	69	67	5th	7th
Collington.....	1.6	19	12	58	64	6th	7th
Penn.....	0.9	16	10	57	47	7th	8th
Washington.....	1.0	35	14	54	61	3rd	5th
Hoosic.....	8.5	61	23	52	63	2nd	5th
Sassafras (loam).....	1.2	18	9	49	63	2nd	5th
Dover.....	2.9	46	18	45	50	2nd	5th
Bermudian.....	1.7	47	19	42	49	2nd	5th
Colts Neck.....	1.2	35	16	41	53	3rd	5th
Lansdale.....	1.5	26	15	41	53	2nd	5th
Chester.....	1.2	22	9	40	49	7th	8th
Merrimac.....	0.8	37	13	33	51	7th	5th
Fox.....	2.1	37	14	32	38	2nd	7th
Gloucester.....	1.5	35	11	29	47	3rd	5th
Hagerstown.....	3.1	61	28	27	50	1st	4th
Whippany.....	1.7	36	13	20	36	1st	5th
Sassafras (loamy sand).....	1.3	36	7	17	29	1st	5th
Sassafras (sand).....	1.6	1290	6	15	34	1st	5th
Papakating.....	2.9	18	10	13	35	2nd	5th
Lakewood.....	1.2	153	4	11	31	1st	5th

\* Limed with dolomite to pH 6.5.

† Same soils and in same order as those shown in table 1.

the chloride to one set of pots at a rate corresponding to 200 pounds of the element per 2 million pounds soil. The Ca-Mg and the Ca-K ratios of the exchange complexes of the soils to which no K and 200 pounds K, respectively, were added are shown in table 2. As a result of the use of dolomitic limestone, the Ca-Mg ratios are entirely out of line with that suggested for the ideal soil, but the Ca-K ratios of the 200-K set of soils approach the ideal fairly closely.

The yields of alfalfa (table 2) were materially increased in 18 of the 20 soils by adjusting the Ca-K ratios to a point approximating the ideal 13:1 ratio. The K content of the first crop of alfalfa was considerably higher than the critical 1 per cent. With the harvesting of successive crops, however, the time soon

arrived with most of the soils when the K content of the crop fell below this level (table 2).

At this point it is necessary to digress for a moment to consider release of cations from the primary minerals in the soil. A further purpose of this study had been to determine the rate at which these soils would continue to yield K to alfalfa. In effect, the roots of the alfalfa plant were substituted for a laboratory extracting solution. The results showed that a number of the soils could supply considerable amounts of K more or less continuously.

In the growing of crop plants we are dealing with two sets of cation equilibria: those in the soil and those in the plant. Within limits, however, the equilibrium in the plant is the product of soil-plant interrelationships. Continued studies of plant cation values revealed that although the content of Ca, Mg, and K varied greatly, in relation both to the nature of the soil and to the number of successive crops harvested, the sum of their equivalents per 100 gm. dry matter for any one harvest was virtually constant for all soils (3). Although this fact had been pointed out by Liebig (4, pp. 64-65), it had been lost sight of until it was again demonstrated by Van Itallie (7) a century later.

Of these three basic cations, Ca is dominant in the soil, whereas K dominates in the plant. Thus only by maintenance of a relatively high Ca-K ratio in the soil can the K content of a plant being grown under conditions of high fertility be kept down where it belongs. Even so, it is difficult to maintain a high content of exchange K in farmed soils, most of them tending to become deficient in this element with continued cropping. The problem involved with K, therefore, is one of maintaining an adequate but not excessive supply in the soil.

If normal alfalfa plants can be grown at a K content of 1 per cent, it is false economy to apply large enough amounts of this element in fertilizer form to allow the plant to take it up to the extent of 3.5 per cent of its dry weight, as has been found possible (5). Ca is a relatively low-cost element, and the soil should be so well supplied with it that the plant roots will have an opportunity to absorb Ca up to the point of diminishing returns from its use. An exchange Ca-K ratio of 13:1 in the soil enables the plant to absorb a liberal margin of K in excess of its requirements and yet not so much as to be a serious waste of the element. Once the soil has been limed and fertilized with K to this point, the problem then resolves itself into one of supplying repeated moderate doses rather than infrequent heavy doses. This applies especially to soils with exchange capacities of less than 10 m.e. per 100 gm. The exchange Ca content of such soils is too low to permit of establishing suitable Ca-K ratios and, at the same time, of having enough K stored in the soil to meet the full-season requirements of the crop.

In connection with these studies it soon became apparent that the Mg-K ratio was even more important than the Ca-K ratio. This was found to apply especially to sandy soils of low exchange capacity and to soils that were being kept acid for the growing of such crops as potatoes. Thus the tendency of plants to take up K at the expense of adequate amounts of Mg was found to be very troublesome under such conditions.



To study this point in detail, the same set of 20 soils was again employed. In this case, however, pure  $\text{CaCO}_3$  was used to raise the pH values to pH 6.5, and Mg was added only as the sulfate. The report on this work (6) showed that, when the Mg content of the exchange complex fell below the ideal 10 per cent saturation, marked response was obtained from use of this element in soluble form. The evidence indicated that this might be more nearly a critical than an optimum value for exchange Mg. Thus alfalfa yields were considerably higher on the whole where much larger amounts of Mg had been added, as in the case where dolomitic limestone was used to correct soil acidity, than when this element was supplied only in controlled and relatively limited amounts by the use of  $\text{MgSO}_4$ .

Although adequate amounts of Mg can be supplied in the form of liming materials, it is not safe to assume that they will be. This method of supplying Mg often fails on sandy soils and for acid-soil crops. It also fails where oyster shells and calcitic forms of lime are used on Mg-deficient soils. So important has this problem become in the New Jersey Coastal Plain area, where large amounts of K are being applied to the soil, that most fertilizer manufacturers now include a soluble form of Mg in the fertilizer mixtures that are offered for sale in these areas.

More recently we have been impressed with the fact that Ca can have a negative as well as a positive value, especially when it comes to occupy too large a percentage of the exchange complex at the expense of H. Thus even though the Ca-Mg, Ca-K, and Mg-K ratios may have been adjusted to supposedly correct values, the Ca-H value still remains to be considered. In the enthusiasm for liming acid soils, the concept has developed that such soils cannot be over-limed, particularly if pulverized limestone is employed. But so many cases of Mn deficiency have been brought to our attention during the last few years that this problem can no longer be ignored. Once the soil has been limed and re-limed to the point that few zones of low pH remain and the whole volume of soil has a pH level beyond 6.5, the problem of deficiencies of Mn and certain other minor elements comes into play. In other words, the exchange-H values in soils of the humid areas are as important as those of the exchange Ca, K, and Mg. Thus a Ca-H ratio of 3.25:1, which is normally obtained at about pH 6.5, has been set as the tentative upper limit for crops, other than those belonging to the perennial deep-rooted group, until such time as the Mn studies that are now under way can be brought to a conclusion.

#### SUMMARY AND CONCLUSIONS

An 8-year study on 20 important agricultural soils of New Jersey, in which use was made of the roots of alfalfa plants as cation-extracting agents, has led to the following conclusions:

Conditions approach the optimum for the cation nutrition of alfalfa when 65 per cent of the exchange complex of the soil is occupied by Ca, 10 per cent by Mg, 5 per cent by K, and 20 per cent by H.

The ratios of the basic nutrient cations in the alfalfa plant bear little resemblance to those in the exchange complex of the soil on which it was grown.

Ca is the dominant cation in the soil and K in the alfalfa plant. The plant tends to take up more K than it needs unless the Ca content of the soil is maintained at a relatively high level.

When the Ca-K ratio in alfalfa tops exceeds 4:1, or when the K content of the tops falls below 1 per cent, marked response to applications of soluble K will normally be obtained.

When any one of the nutrient cations is deficient in the soil, more of the others move into the alfalfa, but the sum of the cation equivalents in the plant per unit weight of dry tissue tends to be a constant.

The tendency of alfalfa to absorb more K than it requires makes it necessary to consider how this can be avoided. K is a much more expensive element than the Ca which it replaces. Furthermore K is of much less importance, quantitatively, than Ca in the nutrition of animals. In soils of low exchange capacity, or in those that are maintained at low pH values for the benefit of acid-soil crops, it would be desirable to apply moderate amounts of K from time to time during the crop season rather than a large amount at the time of planting only. Otherwise the crop will contain an unduly large amount of K.

Mg deficiency tends to be widespread on sandy and acid soils because the liberal applications of K that are normally used under such conditions enable the plant to absorb an excess of K in place of part of the needed Mg.

Liming acid soils to the point where virtually all the exchange H in the entire volume of plowed soil has been replaced by Ca tends to cause a deficiency of Mn in crops other than the deep-rooted perennials, and an increasing number of crop failures are resulting from this practice. This principle also applies to other members of the minor-element group.

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## PROPERTIES THAT INFLUENCE AVAILABILITY OF CALCIUM IN THE SOIL TO PLANTS<sup>1</sup>

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Calcium and hydrogen are the two ions that constitute the greater proportion of the colloidal exchange complex of most humid-region soils. This relatively large quantity of calcium in the cation exchange complex of some of the most productive soils makes it desirable to have more information concerning the factors determining availability to plants of different ions in the soil.

Goldschmidt (19) has drawn attention to the fact that distribution and availability of the various chemical elements were fundamentally controlled by the chemical evolution of our planet during geological time. It has been pointed out that the cosmic abundance of the chemical elements is clearly dominated by general principles of nuclear stability and of nuclear evolution. The important processes of physical and chemical segregation and concentration, however, dominate the history of matter during geochemical evolution according to the properties, not of the nuclei, but of the electronic shell of the various elements. Distribution of the various chemical elements was essentially controlled by their chemical affinity toward oxygen and sulfur and by their latent heat of vaporization. The free energy of oxidation per gram atom of oxygen of the lowest oxides of the electropositive elements and corresponding compounds with sulfur can be taken as suitable measures of their chemical affinities.

Fractional crystallization of silicate magmas is one of the main steps in geochemical evolution connected with cooling of the earth and crystallization of the silicate slag. The process of crystallization involved a sorting or selection of the various atoms or ions according to their sizes, and with regard to their faculty for entering the crystal lattices or spacial network of the different minerals which crystallize from magmatic solutions.

The correlation between biological essentiality and atomic structure of the chemical elements has been pointed out by Steinberger (44). He draws attention to effects of position and number of electrons on the chemical and physical properties of the elements. It is highly desirable that more consideration be given to the known physical and chemical properties of the nutrient elements discussed by Goldschmidt and Steinberger in plant nutrition studies. Many characteristics of the nutrients are related to the energy properties of their ions.

### USE OF ENERGY PROPERTIES OF NUTRIENT IONS IN SOIL FERTILITY AND NUTRITION STUDIES

For a better understanding of some important principles involved in plant nutrition, special consideration must be given to certain energy properties of nutrient ions utilized by plants. One of the principal differences between in-

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organic and organic matter is the stored potential energy in the organic compounds. Every form of energy may be considered as compounded of two factors—one, the intensity factor, and the other, the capacity factor. The data presented are largely concerned with the intensity factor and only incidentally with the capacity or quantity factor. The intensity factor of energy is of primary importance in considering the intensity of removal of cations from soil colloids and the intensity of absorption of certain nutrient cations by some plants. The capacity factor of energy, as expressed in concentration, and the relative solubility of nutrients are important factors in soil-formation processes. The two standard measurements of the factors of energy most likely to be of use in certain studies are the standard electrode potentials and the ionization potentials.

#### *Standard electrode potentials of certain nutrient elements*

The standard electrode potential of certain nutrient elements listed in the International Critical Tables (24) and reported by Kolthoff and Furman (29) and by Hodgman (22) may be helpful in predicting relative availability and absorption of nutrient ions. It has been pointed out by Cooper and Padén (12) that there is a very close correlation between the intensity of removal of cations from soil colloidal complexes and the normal electrode potentials. The intensity of removal of four cations from a composite soil sample electrodialed for the first 2-hour period expressed as percentage of the total quantity of each cation removed in 32 hours of electro dialysis for K, Na, Ca, and Mg was 56.00, 24.66, 17.49 and 11.98 per cent, respectively. The intensity of removal of cations in fractional electro dialysis from homionic soil colloids expressed as percentage of the total amount extracted in the first 2 hours for Rb, K, Na, Li, Ca, and Mg was 91.32, 60.51, 53.43, 43.15, 36.89, and 24.31, respectively. These data clearly illustrate the relation between the relative strength of certain cations and the intensity of their removal from soils by electro dialysis.

#### *Ionization potentials*

Certain ionization potentials of elements in various stages of ionization reported by Millikan and Bowen (36), Noyes and Beckman (37), Latimer and Hildebrand (30), and Hodgman (22) are included in table 1. The equivalent energy required for removal of the last bound electron is given in second column. This arrangement gives very little information on the relative activity of ions other than the monovalent ions such as the alkali metals and hydrogen. The equivalent voltage values found in the third column give a better grouping of the relative activity of ions in their most common atomic ionic valence state. The relative activity expected in this atomic ionic series according to relative strength of ions is Cs, Rb, K, Na, Li, Ba, Sr, Ca, H, Mg, Mn, Fe, etc. In this grouping the hydrogen ion ranks next to calcium in relative strength, and it would be expected that it would predominate over any ion lower in the series. This grouping is in agreement with the established order of activity of certain ions in soil colloidal studies. The ionization potential values in this table would suggest that in the absence of such strong anions as chloride, acetate, sulfate, and nitrate

the elements below hydrogen in the third column would be expected to form complex ions and would not be present in the soil solution in large amounts in atomic form. These ionization values also suggest some of the reasons why it is not possible to remove large quantities of the elements below hydrogen in this series by electrodialysis; whereas, some of the elements below hydrogen can be readily extracted from the soil by addition of relatively strong anions. These strong anions may form complex cations with many of the elements below hydrogen in this series. It is not likely that an element like aluminum, with an inmost normal valence ionization potential of 28.31 volts, would form atomic ions in the soil solution. The solubility and removal of such an element from the soil would

TABLE 1

*Arrangement of atomic ions in order of ionization potential in volts or the intensity of binding of the most common valence electrons*

ORDER OF STRENGTH OF ATOMIC ION	DEGREE OF IONIZATION		
	M <sup>+</sup>	M <sup>++</sup>	M <sup>+++</sup>
Cs.....	3.870		
Rb.....	4.159		
K.....	4.318		
Na.....	5.120		
Li.....	5.363		
Ba.....	5.190	9.95	
Sr.....	5.667	10.98	
Ca.....	6.09	11.82	
H.....	13.53		
Mg.....	7.61	14.96	
Mn.....	7.41	15.70	
Fe.....	7.83	16.16	
Co.....	7.81	17.30	
Zn.....	9.36	17.89	
Cu.....	7.68	20.34	
Al.....	5.96	18.74	28.31

very probably be determined by the relative quantity of strong anions present in the soil.

The relatively low intensity of removal of magnesium from cotton, corn, and soybean tissue in electrodialysis studies reported by Cooper *et al.* (14) suggests that some ions relatively weaker than calcium and stronger than magnesium are involved, which accounts for the apparent delayed removal of magnesium in such studies. The ionization potentials suggest that hydrogen ion would be expected to follow calcium in intensity of removal. The results of electrodialysis studies on humate-treated soil by Toth (45) are in close agreement with the findings from fractional electrodialysis of plant tissue. Available information on intensity of removal of magnesium in electrodialysis studies suggests that structural hydrogen in the organic compounds may be more readily removed than atomic magnesium.



## NATURE AND STABILITY OF CLAY MINERALS

In a review of cation-exchange studies, Wiklander (46) suggested that in most cases soil colloids seem to result from a formation of a number of crystalline clay minerals constituting the main mass of the clay particle, the gel-like silicates with less definite composition, and humus matter. The type of clay mineral predominating in a given mature soil would be expected to be that which is most stable under conditions prevailing in the soil. Since the crystalline state is the most stable one, matter tends to pass from the amorphous into a crystalline state. It has been suggested that clay colloids principally consist of crystalline silicate particles belonging to the montmorillonite, the kaolinite, or the mica mineral group.

The thermodynamic properties determining the direction of the chemical changes seem to be related to the standard free energy of reaction. Spontaneous chemical reactions often proceed in the direction resulting in the largest decrease of free energy. Since the standard electrode potentials and the ionization potentials are energy properties of nutrient ions, they should be useful in predicting the reaction of various ions in soil complexes. Goldschmidt (19) has suggested that the general principle controlling the distribution and association of elements in the process of weathering and the sedimentation cycle is the ionic potential. It is concluded that the ionic potential, which is the quotient of ionic charge and ionic radius, dominates the interaction between the ions and the water molecules.

Large ions with small ionic potentials are likely to be collected in the evaporate, since they are not absorbed in the hydrolyzate because of their strong polarizability, as is the case with potassium rubidium and cesium increasingly in order of increasing radius. In regard to base-exchange phenomena in the hydrolyzate of soils, the similarity of the ionic radii of potassium (1.33A.), ammonium (1.43A.), and hydroxonium (about 1.40A.) seems to be of special geochemical significance.

## LOCATION OR POSITION OF EXCHANGE BONDS

The location or position of the bonding linkages in the exchange complex of soils may influence fixation or release of specific cations. The nature of the secondary clay minerals in the colloidal fraction of the soil affects the degree of hydrolysis of adsorbed cations. Martin *et al.* (33) have suggested that the amount of fixation may depend upon the number of attraction spots that possess special properties either because of position in the clay lattice or because of the nature of the soil mineral. They also suggested that fixation of K, Rb, Cs, and possibly H ions results in a reduction of the total exchange capacity of the soil minerals. They found that in some soils certain cations in the exchange complex can pass from the loosely held to a very strongly held state. Their findings seem to indicate that fixation of potassium includes, first, an adsorption in exchange for other adsorbed cations, and then a fixation which results in a reduction in total exchange capacity of the soil. Cations shown to undergo this change of state were K, Rb, Cs, and possibly H. The cations Li, Na, Ca, Mg, Ba, and  $\text{NH}_4$  were not fixed in the nonreplaceable form by the soil studies. In fractional

electrodialysis studies, Cooper and Paden (12) observed that there was a rather low total percentage removal of added K and Na. The percentage of the added cations extracted for K, Na, Ca, and Mg was 57.65, 75.73, 100, and 93.59, respectively. The intensity of removal of the replaced K and Na by electrodialysis, however, was very high. Exchangeable potassium is very readily removed from certain soil colloids. It has been reported by Toth (45) that additions of phosphate, silicate, and humate anions have increased the exchange capacity of the soil.

In a series of papers on fixation of potassium, Joffe and Levine (25, 26, 27) and Levine and Joffe (31, 32) have reported on difference in the fixation of various cations by soils. Calcium and barium were not fixed; whereas potassium and ammonium were fixed in some soils.

#### SOLUBILITY OF NUTRIENT COMPOUNDS

There is a wide variation in solubility of different nutrient compounds. The solubility data reported in standard reference works have been determined by different investigators under various temperature conditions, therefore it is not possible to make close comparison of the relative solubilities of different nutrient materials. A consideration of the solubility values in grams per 100 ml. of water of the halogen salts of the alkali metals suggests that the salts of isosteric or isoelectronic ions are relatively less soluble than similar salts of nonisosteric ions where there is a greater difference in size of ions. In the fluoride group, lithium and sodium fluorides are least soluble; in the chloride group, potassium chloride, with a solubility value of 34.7 gm. at 20°C., is least soluble; in the bromide group, rubidium bromide would be expected to be least soluble at comparable temperatures; and in the iodide group, cesium iodide, with a solubility value of 44.0 gm. at 0°C., is least soluble.

Among the halogen salts of the alkaline earth metals, however, the reverse seems to be true. The isoelectronic calcium chloride with a solubility value of 59.5 gm. at 0°C., strontium bromide with a value of 204.2 gm. at 0°C., and barium iodide with a value of 200.0 gm. at 15°C. are the most soluble in the respective groups.

The sulfates of the alkali metals are much more soluble than the alkaline earth sulfates. The alkaline earth nitrates seem to be relatively more soluble than the alkali sulfates. The alkali acetates are more soluble than the alkaline earth acetates. These relative solubility values undoubtedly have a significant influence in ion-exchange reactions and in determining availability of nutrients to plants.

Since the relative quantities of carbon dioxide and nitrogen available to plants may determine the differential in the synthesis of carbonaceous or proteinaceous materials, depending upon the relative quantities of the anions of these nutrients available for photosynthetic reactions, the relative solubility of the salts of the alkali metals and ammonium as compared with magnesium and calcium included in table 2 are of special interest in considering the availability of CO<sub>2</sub> for photosynthetic reactions. Bower and Turk (3) have reported that there may be a

deficiency of both calcium and magnesium in alkali soils with a high content of sodium. It is noted that most of the nutrient anion compounds of calcium, with the exception of nitrate and chloride forms, have a relatively low solubility; whereas, potassium, sodium, and ammonium ions form carbonate compounds of relatively high solubility. The solubilities of the bicarbonate and carbonate compounds of the alkali metals are of special interest in this connection. The relatively low solubility of calcium carbonate may be related to the relatively high protein content of certain plants relatively high in calcium. The association of the relatively high potassium requirement of the highly carbonaceous crops may be related to the availability of the bicarbonate ion for photosynthesis in the presence of an adequate supply of such materials as potassium, sodium, or ammonium bicarbonates. The possible relation between the relative solubility of carbonate compounds and their effect in determining the differential in photosynthetic processes in terms of carbonaceous and proteinaceous crops has been

TABLE 2

*Solubility\* of certain nutrient compounds in grams of anhydride per 100 gm. cold water*  
Temperature around 30° or 0°C., as indicated

ION	HCO <sub>3</sub>	CO <sub>3</sub>	C <sub>2</sub> O <sub>4</sub>	OH	SiO <sub>2</sub>	PO <sub>4</sub>	HPO <sub>4</sub>	H <sub>2</sub> PO <sub>4</sub>	SO <sub>4</sub>	NO <sub>3</sub>	Cl
K.....	22.4	112.0	33.0	97.0°	s.	sl.s.	v.s.	33.0	12.0	31.6	34.7
Na.....	6.9°	7.1°	3.7	109.0	s.	28.3	21.9	110.3	19.5°	73.0°	35.7°
NH <sub>4</sub> .....	11.9°	100.0	4.0	42.0	....	...	42.9°	22.7°	70.60°	118.3°	29.7°
Ca.....	....	0.0014	0.00067	0.185°	0.0095	0.002	0.02	1.8	0.298	102.0°	59.5°
Mg.....	....	0.0106	0.07	0.0009	....	0.02	0.31	....	26.0°	42.33	35.3

\*s = soluble, v = very, sl = slightly, i = insoluble.

suggested by Cooper *et al.* (17). It is not probable that a relatively large quantity of calcium bicarbonate would exist in plant sap, as conditions would be favorable for formation of calcium carbonate or organic calcium compounds of relatively low solubility and low energy value. In the presence of large quantities of calcium, the nitrate and the chloride are the only common nutrient anions that would be readily soluble in combination with calcium, and therefore, the synthesis of proteins might be relatively greater than the synthesis of carbohydrates where a limited supply of carbon dioxide is available for photosynthesis. A general survey of the occurrence and assimilation of nitrogen and carbon dioxide has been published by Burstrom (4, 5).

#### PHYLOGENETIC AND ONTOGENETIC CHARACTERISTICS OF PLANTS

Many of the crop plants now grown in forested areas came from a habitat supporting largely a grass or herbaceous native vegetation. The economic or social factors influencing extension of the culture of certain crop plants beyond the regions with optimum physiological growth factors make it desirable to give special consideration to the physiological growth requirements of different crop plants.

Climatic and soil conditions in a natural grassland area are usually favorable for accumulation of adequate or excessive quantities of certain mineral nutrients. Under such conditions certain of the phylogenetic characteristics of plants native to such a habitat may be based largely upon their tolerance to minerals in the soil solution rather than on specific nutrient requirements. Mineral requirements become a major consideration only when the crops are grown in a habitat significantly different from their native environment such as occurs when grassland plants are transferred to native forested areas. Where plants are subjected to excessive quantities of mineral nutrients, phylogenetic characteristics such as selective accumulation and selective exclusion mechanisms very probably protect them from excessive concentration of certain ions.

*Selective accumulation of nutrients by plants*

A number of investigators including Robinson and Edgington (41), Hutchinson (23), Goldschmidt (19), and Mattson and Koutler-Andersson (34) have reported on selective accumulation of certain metals by some plants.

Selective accumulation of calcium in such plants as legumes, cotton, spinach, potato, tobacco, and tomato through the formation of organic compounds of relatively low energy value such as oxalate, malate, and pectate illustrates one possible mechanism protecting the plant from excessive concentration of calcium ions in its tissues. Since such a protective mechanism is probably a more or less fixed phylogenetic characteristic which operates over a wide range of concentration of different metals, it is possible that the efficiency of this mechanism for inactivating certain ions may result in a deficiency of some nutrients found in relatively low concentration in the nutrient media.

*Selective exclusion of nutrients by plants*

In contrast to the mechanism by which excessively absorbed ions are largely inactivated is the less well understood mechanism of selective exclusion of ions not required in the reproduction of plants. Plants in the grass family including such cereal crops as barley and wheat do not absorb large quantities of calcium regardless of the concentration of ions in the nutrient media. Selective exclusion of calcium by certain tissues concerned with reproduction, such as seeds, fruits, tubers, roots, and stems, may be related to the ontogenetic characteristic of plants. Selective exclusion of such ions as sodium, calcium, chloride, and silica is usually accompanied by selective accumulation of such nutrients as magnesium, phosphorus, and nitrogen as in seed and other reproductive tissues. Selective exclusion of such a nutrient as calcium may be an important factor in determining the structure and keeping quality of tubers, roots, and fleshy tissue such as tomatoes and other fruits. It has been observed (28) that treating tomatoes with a dilute solution of calcium chloride produces firmer tissue and improves the appearance of the product. It has been found that it is necessary to have a relatively high pH value of the soil, which usually means a relatively high calcium content in humid-region soils, to get optimum yields and quality of tomatoes. Mattson and Koutler-Andersson (34) reported that the relative amount of cal-

cium in pea seeds significantly affects the cooking qualities of the peas. Pea seeds relatively high in calcium are hard when cooked; whereas, those relatively high in sodium are soft when cooked.

The possibility of a correlation between the effects of the more or less fixed ontogenetic characteristics in the selective exclusion of calcium and the poor structure and keeping quality of fruit tissues grown on soils relatively low in available calcium suggests the desirability of a careful consideration of this subject.

The citric, malic, and oxalic acids in the mature leaves, peel, and juice of mature fruit of the Valencia orange reported by Sinclair *et al.* (42) illustrate the differential in the exclusion of these acids in the peel and the juice. The citric acid is concentrated in the juice, and the malic and oxalic acids are concentrated in the leaves. Attention has been directed by Wittwer *et al.* (47) to the fact that additional increments of calcium supplied to cultures low in phosphorus accentuated the phosphorus deficiency. A more detailed discussion of this subject will be included in another section of this paper.

#### DIFFERENTIAL IN COMPOSITION OF PLANTS GROWN ON SAME SOIL

The composition of cotton and wheat plants grown on soils with identical or similar fertilizer treatments, shown in table 3, illustrates the difference in the mineral nutrition of plants grown under very similar conditions. The different nutrients are arranged in order of the relative strength of ions, which makes it easier to observe the selective accumulation or selective exclusion of certain elements. It is noted that the cotton plant contains a relatively large quantity of calcium and may be considered a calcium-accumulator plant. The relatively low content of silicon as compared with the wheat straw would suggest that cotton may selectively exclude silicon. The wheat plant contains about one-twentieth as much calcium and more than eight times as much silicon as the cotton plant. Wheat may be considered as a silicon-accumulator. The chemical composition of the cotton plant is more closely correlated with the ion concentration, as expressed in the percentage of the ions in the cation exchange complex of soils, than is the composition of the wheat plant. A consideration of the relative quantity of the exchangeable cations in the soil complex would suggest that wheat may be far more selective in the nutrients absorbed than is the cotton plant. These data suggest the importance of a more detailed consideration of the relation between the relative quantity of ions in the exchange complex of soils and their effect upon the chemical composition of different plants.

Many investigators including Osterhaut (38), Hoagland (21), Cooper and Blink (18), Reed and Haas (40), Collander (7), Cooper *et al.* (8-17), and Snider (43) have considered the selective absorption of certain nutrients by some plants. The general interest in this subject by various investigators suggests the need for more comprehensive research along this line.

#### EXCHANGEABLE CATIONS AND YIELDS OF CROPS AT FOUR SOIL PH LEVELS

In a group of papers by Cooper *et al.* (8-17) the relation of the relative strength of nutrient ions to the chemical composition of plants has been given special con-



TABLE 3  
Yields and chemical composition of cotton and wheat grown on plots receiving different fertilizer treatment on Norfolk fine sandy loam,  
Pee Dee Experiment Station, Florence, S. C.  
Metallic nutrients arranged according to relative strength of ions as indicated by normal electrode potentials

ELEMENTS ARRANGED IN ORDER OF ELECTROLYTIC SOLUTION PRESSURE OR INTENSITY OF ION FORMATION																
PLOT NUMBER	TREATMENT	pH VALUE	YIELDS PER ACRE	K	Na	Ca	Mg	Al	Mn	Fe	Si	S	P	Cl	N	Ash
				+2.92	+2.70	+2.50	+1.55	+1.30	+1.10	+0.43	—	-1.69*	-1.70*	-1.36	-1.69*	
				Standard electrode potentials of above metals in equivalent volts												
Per cent of different nutrient elements in dry matter of plant																
Cotton																
18	0-0-4 lime	6.7	1193	0.92	0.37	2.34	0.747	0.025	0.007	0.049	0.087	0.23	0.447	0.40	2.22	10.06
23	4-8-4 lime	6.5	1723	0.62	0.42	2.43	0.657	0.012	0.027	0.050	0.066	0.33	0.339	0.73	2.45	11.19
24	4-8-4 ...	5.7	1860	0.80	0.43	1.85	0.607	0.024	0.009	0.043	0.074	0.41	0.289	0.58	2.03	9.83
31	0-0-0 ...	5.1	651	0.53	0.38	1.82	0.469	0.034	0.015	0.050	0.134	0.25	0.259	0.46	2.13	8.19
36	2-8-4 ...	5.2	1669	0.59	0.34	1.28	0.218	0.014	0.051	0.037	0.073	0.42	0.242	0.68	1.25	7.68
39	4-8-8 ...	5.3	1749	1.05	0.70	1.24	0.180	0.021	0.027	0.035	0.068	0.42	0.200	0.81	1.42	8.57
43	6-6-8-4 ...	5.4	1854	0.87	0.73	1.44	0.200	0.011	0.030	0.080	0.087	0.42	0.203	0.77	1.66	8.31
Average.....				0.78	0.48	1.77	0.448	0.020	0.024	0.049	0.084	0.35	0.283	0.63	1.88	9.12
Per cent of K.....				100.00	61.54	226.92	57.44	2.56	3.08	6.28	10.77	44.87	36.28	80.77	241.03	1169.23
Milliequivalents.....				19.95	20.87	88.32	36.84	2.21	0.87	1.76	11.97	21.83	27.40	17.77	402.57	....
M.e. expressed as per cent of K.....				100.00	104.61	442.71	184.66	11.08	4.36	8.82	60.00	109.42	137.34	89.07	2017.89	....
M.e. expressed as per cent of N.....				4.96	5.18	21.94	9.15	0.55	0.22	0.44	2.97	5.42	6.81	4.41	100.00	....
Wheat																
Straw.....				0.208	0.676	0.128	0.077	0.0098	0.066	0.0090	1.01	0.148	0.106	0.507	0.53	4.43
Grain.....				0.189	0.103	0.040	0.146	0.0054	0.048	0.0044	0.35	0.155	0.427	0.101	1.72	1.96
Average.....				0.199	0.390	0.084	0.112	0.0076	0.057	0.0067	0.68	0.152	0.267	0.304	1.13	3.20
Per cent of K.....				100.00	195.98	42.21	56.28	3.82	28.64	3.37	341.71	76.38	134.17	152.76	567.84	1608.04
Milliequivalents.....				5.09	16.96	4.19	9.21	0.85	2.08	0.24	96.94	9.48	25.85	8.57	241.97	....
M.e. expressed as per cent of K.....				100.00	333.20	82.32	180.94	16.70	40.86	4.72	1904.52	186.25	507.86	168.37	4753.83	....
M.e. expressed as per cent of N.....				2.10	7.01	1.73	3.81	0.35	0.86	0.10	40.06	3.92	10.63	3.54	100.00	....

\* Discharge potential of acids.  
† Average for eight fertilizer treatments.

sideration. Further experiments were conducted on Cecil sandy loam to study the yield and chemical composition of crop plants receiving different fertilizer treatments on soil adjusted to four different pH levels. The data in table 4 record the 5-year average yields of seed cotton and 1 year of Kobe lespedeza hay harvested from 26 plots at each of the four pH levels indicated. There is a consistent increase in yield of cotton and lespedeza hay with increase in pH of the soil. The quantity of exchangeable K, Na, Ca, Mg, and H and the percentage saturation of the soil by the various metallic ions at different pH levels are also recorded in table 4. The total milliequivalents of exchangeable cations per 100 gm. of soil at the four pH levels varied from 5.97 to 6.08 with an average of 6.05. Hydrogen in the exchange complex ranged from 36.85 to 70.72 per cent with an average of 52.07 per cent, while Ca saturation ranged from 8.72 to 34.67 per cent with an average of 22.82 per cent, and K ranged from 6.91 to 11.04 per cent with

TABLE 4  
*Yields of seed cotton and lespedeza hay and content of exchangeable cations in soil complexes at different pH levels*

pH VALUE	YIELDS PER ACRE		K		Na		Ca		Mg		H		TOTAL EX- CHANGE- ABLE CATIONS
	Seed cotton	Lespe- deza hay	Total		Total		Total		Total		Total		
			m. e.*	per cent†	m. e.	per cent	m. e.	per cent	m. e.	per cent	m. e.	per cent	
5.0	1199	2875	0.42	6.91	0.51	8.39	0.53	8.72	0.32	5.26	4.30	70.72	6.08
5.5	1340	3425	0.67	11.04	0.47	7.74	1.17	19.27	0.36	5.93	3.40	56.01	6.07
6.0	1416	4227	0.67	11.02	0.48	7.89	1.74	28.62	0.49	8.06	2.70	44.41	6.08
6.5	1444	4441	0.56	9.38	0.49	8.21	2.07	34.67	0.65	10.89	2.20	36.85	5.97
Ave.	1350	3742	0.58	9.59	0.49	8.10	1.38	22.82	0.45	7.44	3.15	52.07	6.05

\* M.e. = per 100 gm. soil.

† Per cent = of total exchangeable cations.

an average of 9.59 per cent. The saturation percentages for Na and Mg in the exchange complex were only slightly lower than the values for K.

The chemical composition of the cotton plants, expressed as percentage of the plant, in table 5 shows that there is a correlation between the nutrient constituents found in the cotton plant and the quantity of the ion in the soil exchange complex. These data suggest that the relative strength of ions may be a much more significant factor than their concentration, as expressed in the percentage of soil saturation with different ions, in determining absorption and utilization of nutrients. Reed and Haas (40) found that a given concentration of an ion in the nutrient solution is reflected in the amount of that ion in the plant, but the variation is not proportional. Their data also suggest that the relative strength of ions in water cultures may be a far more significant factor than the concentration of ions in the nutrient medium in determining the quantity of an ion absorbed by certain plants. The data in table 5 show a rather wide variation in the quantity of K and Ca in the plants. The total percentage of all four cations decreased with

an increase in the pH value of the soil. The total of the four cations ranges from 4.59 per cent at pH 5.0 to 3.53 per cent at pH 6.5. This relation might be expected, as the total ash content of plants may be relatively low where conditions are nearly optimum for growth. There was not a wide variation in the percentage of the various nutrients at different pH levels.

The data in table 5 also express the chemical composition of the cotton plant in milliequivalents per 100 gm. of air-dry material. These values give a clearer

TABLE 5

*Yield and chemical composition of cotton plants grown at different pH levels*  
Composition expressed as percentage of plant and milliequivalents per 100 gm. air-dry material

pH VALUE	YIELD OF SEED COTTON PER ACRE	K				Na				Ca				Mg				TOTAL	
		% of Plant	% of Total	m.e.	% m.e.	% of Plant	% of Total	m.e.	% m.e.	% of Plant	% of Total	m.e.	% m.e.	% of Plant	% of Total	m.e.	% m.e.		
	lbs.																	per cent	m.e.
5.0	1199	2.28	49.67	58.31	31.64	0.109	2.37	4.74	2.57	1.85	40.31	92.50	50.19	0.350	7.63	28.73	15.59	4.59	184.33
5.5	1340	1.91	48.11	48.85	30.38	0.108	2.72	4.70	2.92	1.64	41.31	82.00	51.00	0.307	7.73	25.25	15.70	3.97	160.80
6.0	1416	1.69	44.71	43.22	26.96	0.084	1.69	2.78	1.73	1.63	43.12	81.50	50.84	0.399	10.56	32.81	20.47	3.78	160.31
6.5	1444	1.55	43.91	39.64	26.36	0.082	1.76	2.70	1.80	1.53	43.34	76.50	50.86	0.384	10.88	31.58	21.00	3.53	150.42
Ave.	1350	1.86	46.85	47.51	29.00	0.086	2.17	3.73	2.27	1.66	41.81	83.13	50.69	0.360	9.07	29.61	18.05	3.97	163.97

TABLE 6

*Ratios of percentages of certain constituents of cotton plants to percentages of various cations in the exchange complex of soils at different pH levels*

pH VALUE	YIELD OF SEED COTTON PER ACRE	PER CENT OF PLANT				PER CENT OF M.E. IN PLANTS			
		K	Na	Ca	Mg	K	Na	Ca	Mg
	lbs.								
5.0	1199	7.19	0.28	4.62	1.45	4.58	0.31	5.76	2.96
5.5	1340	4.36	0.35	2.14	1.30	2.75	0.38	2.65	2.65
6.0	1416	4.06	0.21	1.51	1.31	2.45	0.22	1.78	2.54
6.5	1444	4.68	0.21	1.25	1.00	2.81	0.22	1.47	1.93
Ave.....	1350	4.89	0.27	1.48	1.20	3.02	0.28	2.22	2.39

picture of the nutrient requirements of plants than can be obtained from data expressed as percentages of the plant. The average percentages of Ca, K, Mg, and Na are 50.69, 29.00, 18.05, and 2.27, respectively.

The ratios of the percentages of certain constituents in the cotton plant to the percentages of the various cations in the exchange complex of the soil are expressed in table 6. The ratios are expressed as percentages of plant and percentages of milliequivalents in the plant. These ratios illustrate the selective absorption of K, as the proportion of this element in the plant is larger than the

relative proportion of K ions in the exchange complex of the soil. The K ratios expressed as percentage of plant ranged from 7.19 to 4.06 with an average of 4.89. The ratio values for Ca ranged from 4.62 to 1.25 with an average of 1.48. The average value for Mg is 1.2. The ratios based on milliequivalent values are smaller but show the same general relationship, with the exception of Mg, the values of which are relatively higher. These values suggest that cotton plants absorbed a higher proportion of Mg than of Ca. In interpreting this table it is helpful to consider that the average percentage of Ca in the exchange complex of the soil was 22.82 as compared with 7.44 for Mg. At the lower percentage saturation there may be a higher proportion of certain ions removed by the plant.

The relative proportion of the four nutrients removed from the varying degrees of ion saturation in the cation exchange complex at the four pH levels can be seen by comparison of data in tables 4 and 5. The ratios of cations in the plant to

TABLE 7

*Yields of seed cotton, corn, and wheat and exchangeable cations in the exchange complex of the soil with different fertilizer treatments, Pee Dee Experiment Station, Florence, S. C.*

PLOT NUM- BER	TREATMENT	pH VALUE	YIELD PER ACRE			K		Na		Ca		Mg		H		TOTAL EX- CHANGE- ABLE CATIONS
			Seed Cot- ton	Corn	Wheat											
			lbs.	bu.	bu.	m.e.*	per cent†	m.e.	per cent	m.e.	per cent	m.e.	per cent	m.e.	per cent	
18	0-0-4 lime	6.7	1193	32	13.8	0.15	5.62	0.14	5.24	1.78	66.67	0.45	16.85	0.15	5.62	2.67
23	4-8-4 lime	6.5	1722	51	33.2	0.18	4.47	0.16	3.97	2.83	70.22	0.44	10.92	0.42	10.42	4.03
24	4-8-4 ....	5.7	1860	48	33.1	0.17	6.05	0.15	5.34	1.57	55.87	0.20	7.12	0.72	25.62	2.81
31	0-0-0 ....	5.1	651	24	10.5	0.06	3.39	0.11	6.21	0.55	31.07	0.12	6.78	0.93	52.54	1.77
36	2-8-4 ....	5.2	1669	39	20.8	0.15	5.64	0.11	4.13	0.75	23.19	0.13	4.89	1.52	57.14	2.66
39	4-8-8 ....	5.3	1749	41	23.7	0.21	9.55	0.14	6.36	0.80	36.36	0.12	5.45	0.93	42.27	2.20
43	6.6-8-4 ....	5.4	1854	41	32.6	0.08	4.06	0.12	6.09	0.76	38.58	0.16	8.12	0.85	43.15	1.97
Average.....			1528	39	24.0	0.14	5.43	0.13	5.04	1.29	50.00	0.23	8.91	0.79	30.62	2.58

\* m.e. = per 100 gm. soil.

† per cent = of total exchangeable cations.

those in the soil were 3.02 for K, 0.28 for Na, 2.22 for Ca, and 2.39 for Mg. The relatively low values for Na and Ca suggest that a relatively small proportion of the exchangeable ions are removed from the soil by this crop. Mehlich and Reed (35) also noted the selective accumulation of calcium by cotton plants as expressed in the Ca:K ratio in the plant.

#### YIELDS AND CHEMICAL COMPOSITION OF COTTON GROWN ON ORANGEBURG SANDY LOAM AND NORFOLK FINE SANDY LOAM

The data from soil fertility experiments begun in 1914 and continued with slight modifications to date are of special interest in plant nutrition studies. Each of the fertilizer treatments was 1,000 pounds per acre annually of the analyses indicated. The continuous fertilizer treatment over the 33-year period has resulted in a significant change in crop yields, soil reaction, and percentage of the cations in the exchange complex of the soil. These differences are shown in table 7. The average yields of seed cotton varied from 651 to 1,860 pounds per

acre with a mean value of 1,528 pounds. The average corn yields varied from 24 to 51 bushels, and the wheat yields from 10.5 to 33.2 bushels per acre. The proportion of the exchangeable cations in the soil varied widely with the different treatments. There was a much wider variation in exchangeable H than in the other cations. The H saturation in the exchange complex varied from 5.62 per cent for the 0-0-4 fertilizer and lime treatment to 57.14 per cent for the 2-8-4 fertilizer plots. The percentage calcium saturation varied from 28.19 to 70.22 per cent. The average cation saturation for Ca, H, Mg, K, and Na was 50.00, 30.62, 8.91, 5.43, and 5.04 per cent, respectively.

The relation of crop yields to the percentage cation saturation of the soil is also shown in table 7. A comparison of the cotton yield on plot 23 (containing 10.42 per cent H saturation) with that of plot 36 (containing 57.14 per cent H saturation) does not suggest that there is a close correlation between the percentage of H in the soil exchange complex and the yield of cotton. Likewise, there seems to be no close correlation between cotton yields and percentage calcium saturation.

With the exception of plots 18 and 31, which did not receive a complete fertilizer treatment, there seems to be a direct relation between wheat yields and percentage saturation of calcium, and an inverse relation between wheat yields and percentage of H in the ion exchange complex of the soil. The wheat yields on soil with percentages of calcium saturation of 70.72, 55.87, 38.58, 36.36, and 28.19 were 32.2, 33.1, 32.6, 23.7, and 20.8 bushels per acre, respectively. The corn yields at the same degrees of calcium saturation were 51, 48, 41, 41, and 39 bushels per acre, respectively.

The percentage saturation of K and Na does not seem to be closely correlated with yields of crops on these soils.

In contrast to the conventional method of expressing the mineral chemical composition of plants in terms of the oxide of the element, expressing the composition in terms of milliequivalents, which represent the combining capacities of the nutrients, presents a much clearer picture of the nutrient requirements of different plants grown under various conditions. The data in table 8 express the composition in terms of milliequivalents and are comparable with the data in table 3. The data in milliequivalents give a different order of magnitude of nutrients from the percentage composition values. The sodium content is slightly higher than the potassium content. The calcium and magnesium contents are higher than either the potassium or the sodium content. There is not a wide variation in the nonmetallic nutrients, with the exception of nitrogen, which is very high. There is a wide difference in the sodium content of the cotton plants grown on Cecil sandy loam, Orangeburg fine sandy loam, and Norfolk fine sandy loam. As shown in table 5 the average amount of sodium in cotton on Cecil sandy loam was 3.73 m.e.; whereas the average content of this element in cotton grown on Orangeburg fine sandy loam and Norfolk fine sandy loam was 20.96 m.e. per 100 gm. of plant material. The sodium content of the cotton plants on the Orangeburg and Norfolk soils was obtained by difference after determination of the potassium content.



Table 9 gives the quantity of each of the four important metallic nutrients, expressed first as percentage of the plant and percentage of the sum of the four cations, and second as milliequivalents in the plant and percentage of the sum of the milliequivalents of all four metals. If the limed plots and the plot that received no fertilizer are excepted, there is a progressive decrease in total milliequivalents, ranging from 182.95 to 111.69 with decreasing yields.

Previous consideration has been given to the constancy of the sum of milliequivalents of K, Na, and Ca in the cotton plant where the total yields and the soil reaction were at comparable levels (15). The data in table 9 suggest that the concept of the constancy of cation equivalents in plants may not be applicable where there is a wide variation in hydrogen-ion concentration in the nutrient media. Since the hydrogen and calcium ions may account for 75 to 80 per cent of the cation saturation in many soils and because of the reciprocal relationship

TABLE 8

*Chemical Analysis of Cotton Plants Grown on soil with Different Fertilizer Treatments, Pee Dee Experiment Station, Florence, S. C.*

Analysis expressed as milliequivalents per 100 gm. of air-dry matter

PLOT NO.	TREATMENT	pH VALUE	YIELDS OF SEED COTTON PER ACRE	K	Na	Ca	Mg	Al	Mn	Fe	Si	S	P	Cl	N	TOTAL
			lbs.	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.
18	0-0-4 lime	6.7	1193	23.53	16.11	116.80	61.43	2.77	0.255	1.76	12.40	14.35	43.23	11.28	475.37	779.29
23	4-8-4 lime	6.5	1723	15.86	18.28	121.29	54.03	1.33	0.983	1.79	9.41	20.59	32.79	20.59	524.63	821.57
24	4-8-4 ....	5.7	1880	21.99	18.72	92.34	49.92	2.66	0.328	1.54	10.55	25.58	27.95	16.36	434.69	702.63
31	0-0-0 ....	5.1	651	13.55	16.54	90.84	38.57	3.77	0.546	1.79	19.10	15.60	25.05	12.97	456.10	694.43
36	2-8-4 ....	5.2	1669	15.09	14.80	63.89	17.93	1.55	1.857	1.33	10.41	26.20	23.40	19.18	267.67	463.31
39	4-8-8 ....	5.3	1749	26.85	30.47	61.89	14.80	2.33	0.983	1.25	9.69	26.20	19.34	22.84	304.07	520.71
43	6.6-8-4 ....	5.4	1854	22.25	31.78	71.87	21.38	1.22	1.092	2.87	12.40	26.20	19.63	21.71	355.46	587.86
Average.....			1528	19.87	20.96	88.42	36.87	2.23	0.863	1.76	11.99	22.10	27.34	17.85	402.57	652.83

involved between hydrogen and calcium, the hydrogen ions cannot be left out of consideration in a study of the total equivalent cation content absorbed by certain plants. The total equivalent cation constancy, not including hydrogen, may be fairly satisfactory where the pH value of the nutrient media is high or the hydrogen-ion concentration is fairly constant. The ionization potential values for hydrogen included in table 1 definitely suggest that the hydrogen-ion concentration must be reduced to a low level or the hydrogen must be taken into consideration in determining the total equivalent cation content of plants. Since there is no simple satisfactory way of determining whether the hydrogen in plants is derived from water or the soil complex, the total cation constancy concept may be of little value in considering the total cation content of plants grown on media with a wide variation in hydrogen-ion concentration.

The intensity of absorption of certain nutrients as expressed in the ratio of percentage of certain nutrients in the cotton plant to percentage of the various cations in the exchange complex of the soil with different treatments is shown in table 10. The ratios are expressed as percentage of plant and percentage of

TABLE 9  
Yield and chemical composition of cotton plants grown with different fertilizer treatments,  
Pee Dee Experiment Station, Florence, S. C.

Composition expressed as percentage of plant and milliequivalents per 100 gm air-dry material

PLOT NUMBER	TREATMENT	pH VALUE	YIELD OF SEED COTTON PER ACRE	K			Na			Ca			Mg			TOTAL					
				% of Plant	m.e.	% m.e.	% of Plant	m.e.	% m.e.	% of Plant	m.e.	% m.e.	% of Plant	m.e.	% m.e.						
			<i>lbs.</i>																		
18	0-0-4 lime	6.7	1193	0.92	21.00	23.53	10.80	0.87	8.45	16.09	7.39	2.34	53.42	116.80	53.61	0.747	17.05	61.43	28.20	4.38	217.85
23	4-8-4 lime	6.5	1723	0.62	15.01	15.86	7.57	0.42	10.17	18.26	8.72	2.43	53.84	121.29	57.91	0.657	15.91	54.03	25.70	4.13	209.44
24	4-8-4	5.7	1860	0.86	22.93	21.90	12.02	0.43	11.47	18.70	10.22	1.85	49.33	92.34	50.47	0.607	16.19	49.92	27.28	3.75	182.95
31	0-0-0	5.1	651	0.53	16.56	13.55	8.50	0.38	11.88	16.52	10.36	1.82	56.88	90.84	56.95	0.469	14.66	38.57	24.18	3.20	159.48
36	2-8-4	5.2	1669	0.59	24.28	15.09	13.51	0.34	13.99	14.78	13.23	1.28	52.67	63.89	57.19	0.218	8.67	17.03	16.05	2.43	111.69
39	4-8-8	5.3	1749	1.05	33.12	26.85	20.04	0.70	22.08	30.44	22.72	1.24	39.12	61.89	46.18	0.180	5.68	14.80	11.04	3.17	133.98
43	6-6-8-4	5.4	1854	0.87	26.36	22.25	15.11	0.73	22.12	31.74	21.56	1.44	43.64	71.87	48.80	0.260	7.88	21.38	14.52	3.30	147.24
Average.....			1528	0.78	22.41	19.87	11.96	0.48	13.79	20.93	12.60	1.77	50.86	88.42	53.24	0.448	12.87	36.87	22.20	3.48	166.09

milliequivalents in the plant. The ratios in both groups clearly demonstrate selective absorption of the stronger potassium and sodium ions. These data suggest that the relative strength of ions may be far more important than the concentration of exchangeable cations in the soil in determining the intensity of absorption of different nutrients.

Ratios for average milliequivalents of several metallic cations in the cotton plant (table 9) to those in the soil on which it was grown (table 7) were found to be 2.20 for K, 2.50 for Na, 1.06 for Ca, and 2.49 for Mg. These, like the data in table 10, indicate selective absorption of the stronger nutrient ions, probably on the basis of relative strength of ions rather than relative concentration of ions as expressed in percentage of the different exchangeable ions.

TABLE 10

*Intensity of absorption of certain nutrients as expressed in the ratio of percentage of certain constituents in cotton plants to percentage of the various cations in the exchange complex of soil with different treatments, Pee Dee Experiment Station, Florence, S. C.*

PLOT NO.	TREATMENT	pH VALUE	YIELD OF SEED COTTON PER ACRE  lbs.	PER CENT OF PLANT				PER CENT OF M.E. IN PLANTS			
				K	Na	Ca	Mg	K	Na	Ca	Mg
18	0-0-4 lime	6.7	1193	3.74	1.61	0.80	1.01	1.92	1.41	0.80	1.08
23	4-8-4 lime	6.5	1723	3.36	2.56	0.84	1.46	1.69	2.30	0.82	2.36
24	4-8-4	5.7	1860	3.79	2.15	0.88	2.27	1.99	1.91	0.90	3.83
31	0-0-0	5.1	651	4.88	1.91	1.83	2.16	2.51	1.67	1.83	3.57
36	2-8-4	5.2	1669	4.30	3.39	1.87	1.83	2.39	3.20	2.03	3.28
39	4-8-8	5.3	1749	3.47	3.47	1.08	1.04	2.10	3.57	1.27	2.02
43	6.6-8-4	5.4	1854	6.49	3.63	1.13	0.97	3.72	3.54	1.26	1.79
Averages.....			1528	4.13	2.74	1.02	1.44	2.20	2.50	1.06	2.49

## CHEMICAL COMPOSITION OF WHEAT

Average values obtained from the chemical analysis of eight samples of wheat plants grown on the same or similarly treated plots as the cotton show some very interesting contrasts with the composition of the cotton plants. Data in table 7 for wheat plants grown with complete fertilizer show that the yields increased directly with the increase in the percentage of calcium in the soil colloidal complex. The data in table 11 show that the wheat plant contains a very low amount of calcium. These data suggest that the growth of wheat is favored by a relatively large quantity of calcium in the soil, but that large amounts of calcium are not absorbed by wheat plants. It is interesting to note the relatively large quantity of sodium in the wheat straw—more than three times that of potassium; whereas in the seed there is almost twice as much potassium as sodium. The data in table 11 suggest that there may be a selective accumulation of sodium and silicon in the wheat straw and of magnesium, phosphorus, and nitrogen in the seed. The seeds, when compared with the straw, seem to selectively exclude sodium, calcium, silicon, and chlorine.

The differential in the chemical composition of different wheat tissues as indicated by ratios of nutrients in the tissues is shown in table 12. These ratios show some interesting relations. Comparison of the vegetative tissue ratios with those of the seeds indicates the elements selectively excluded by the seed. The relatively low fractional value for certain ratios indicates that the lower member in the comparison is selectively excluded from the seed, or that the upper member is selectively accumulated. The ontogenetic and phylogenetic significance of the exclusion of such strong ions as calcium and chlorine by seedlings has been discussed by Cooper *et al.* (17). It is suggested that selective ex-

TABLE 11

*Selective accumulation and selective exclusion of certain nutrients in vegetative tissue and seeds of wheat, Pee Dee Experiment Station, Florence, S. C.*

Results, in percentage of air-dry material, are average values for eight samples

TISSUES	METALLIC ELEMENTS							NONMETALLIC ELEMENTS				
	K	Na	Ca	Mg	Al	Mn	Fe	Si	S	P	Cl	N
Cereal straws.....	.208	.676	.128	.077	.0098	.066	.0090	1.01	.148	.106	.507	0.53
Cereal grain.....	.189	.103	.040	.146	.0054	.048	.0044	0.35	.155	.427	.101	1.72
Average.....	.199	.390	.084	.112	.0076	.057	.0067	.068	.152	.267	.304	1.13

TABLE 12

*Differential in chemical composition of different wheat tissues as indicated by ratio of nutrients in tissues*

RATIO	$\frac{K}{Ca}$	$\frac{Na}{Ca}$	$\frac{Ca}{Mg}$	$\frac{Ca}{Si}$	$\frac{Ca}{S}$	$\frac{Ca}{P}$	$\frac{Ca}{Cl}$	$\frac{Ca}{N}$	$\frac{K}{Si}$	$\frac{K}{S}$	$\frac{K}{P}$	$\frac{K}{Cl}$	$\frac{K}{N}$	$\frac{N}{Si}$	$\frac{N}{S}$	$\frac{N}{P}$	$\frac{N}{Cl}$
Ratio in vegetative tissue.....	1.63	5.28	1.66	.127	0.86	1.21	0.25	.242	.206	1.41	1.96	0.41	.392	0.52	3.60	5.0	1.0
Ratio in seed.....	4.73	2.58	0.27	.114	0.26	0.09	0.40	.023	.540	1.22	0.44	1.87	.110	4.91	11.10	4.0	17.0
Ratio of vegetative ratio to seed ratio	0.34	2.05	6.15	1.11	3.31	13.4	0.63	10.5	0.38	1.16	4.45	0.22	3.56	0.11	0.32	1.25	0.06

clusion of calcium and selective accumulation of magnesium in seeds may be related to assimilation of phosphorus by seedling plants. It is probable that magnesium phosphate is the most stable phosphate compound that could be assimilated by the energy available to seedling plants through respiration and oxidation. The quality of energy resulting from respiration and oxidation would not be sufficient for ready assimilation of phosphorus in as stable a compound as calcium hydrogen phosphate. In studies on the buffer systems of cells, Burstrom (6) suggested that the relatively high pH value of the sap of the wheat plant may be an important factor in determining the intensity of absorption of different ions.

Data on the chemical composition of pecan hulls, shells, and kernels, reported by Hammar and Hunter (20), show that calcium is selectively excluded from the

kernels. The average amount of calcium for the different dates of harvest for kernels, shells, and shucks was 0.09, 0.56, and 0.75 per cent, respectively. The data clearly illustrate the selective accumulation of phosphorus and nitrogen and the selective exclusion of calcium by pecan kernels. The average percentage of phosphorus in the kernels, shells, and shucks was 0.35, 0.03, and 0.21, respectively, and the percentage of nitrogen was 1.97, 0.31, and 1.11, respectively.

Data presented by Beeson *et al.* (2) show the selective exclusion of calcium by tomato fruit. Analysis of their data shows that the average composition of tomato leaflets grown with a comparable supply of various nutrients contained 0.72, 2.55, and 1.72 m.e. (per gram of dry weight), respectively, of K, Ca, and Mg, whereas the tomato fruit contained 64.87, 4.37, and 13.8 m.e. (per kilogram of fresh weight), respectively, of these elements.

Investigation by Kertesz *et al.* (28) showed that the addition of calcium chloride improved the firmness of the fruit and appearance of canned tomatoes. Powers *et al.* (39) found that addition of calcium salts as a firming agent was very effective in preventing fresh, canned, and frozen sliced McIntosh apples from becoming excessively soft or mushy when baked in a pie.

The widespread selective exclusion of calcium by seeds, roots, tubers, and fruits may be an important factor in the structure and keeping quality of tuber, root, and fruit crops grown on soils relatively low in available calcium. The soft structure and the poor keeping quality of some of our perishable crops very often result in serious financial losses to producers due to spoilage.

#### SUMMARY

Calcium and hydrogen ions constitute the greater proportion of the colloidal exchange complex of most humid-region soils. The relatively large quantity of calcium in the cation exchange complex is one of the controlling factors in soil fertility. Distribution and combination of the various elements seem to be related to the process of crystallization involving a sorting or selection of the atoms or ions according to their size and with regard to their faculty for entering the crystal lattice or spacial network of the different mineral compounds. The important processes of physical and chemical segregation and concentration of elements are largely determined by the properties of the electronic shells of the various elements.

Since the energy properties of the various elements are largely determined by the intensity of binding of electrons in the outer electronic shell, it is helpful to consider some of the important energy properties of various nutrients. The intensity factor of energy seems to be far more significant in most biological processes than the capacity or quantity factor. The two standard measures of the intensity factor of energy most likely to be of use in certain biological processes are the standard electrode potentials and the ionization potentials.

The intensity of removal of cations from soil colloids and plant tissue is closely correlated with the standard electrode and the ionization potentials. The total quantity of an ion available is significantly affected by the type of clay mineral predominating in a given soil. The position of exchange bonds may signifi-



cantly affect the fixation and availability of certain nutrient ions. The position of the ion exchange bonds in many soils is apparently not suitable for fixation of large quantities of strong divalent cations such as calcium, strontium, and barium. The nature of the exchange bonds seems to be more suitable for fixation of some of the strong monovalent cations such as potassium, rubidium, and cesium.

Solubility values of soil constituents seem to be more closely related to soil-formation processes and accumulation of nutrients in the soil than to quantity of individual ions absorbed by plants grown on different soils.

The phylogenetic and ontogenetic characteristics of crop plants seem to have been developed as a result of tolerance to concentration of soil nutrients rather than on the basis of requirements. The problem of mineral requirements of crop plants becomes a major factor only when crop plants are grown in a situation significantly different from their native habitat, such as occurs when grassland plants are grown in a forested area.

The selective accumulation and selective exclusion mechanisms are very probably more or less fixed phylogenetic or ontogenetic protective characteristics of plants. The selective accumulation of certain elements by plants is often associated with formation of organic compounds of relatively low solubility and low energy value such as calcium oxalate, malate, and pectate. The selective exclusion mechanism is not well known but in certain cases may be related to the pH value of the plant sap.

A comparison of the chemical composition of cotton and wheat plants grown on the same soil with the same or similar fertilizer treatments shows a marked contrast in the mineral content of plants. The metallic nutrients in all tabulations are arranged in order of the relative strength of ions as indicated in standard electrode potentials.

The cotton plant contains a relatively large quantity of calcium and may be considered a calcium-accumulator. Its relatively low content of silicon as compared with wheat straw would suggest that the cotton plant selectively excludes silicon. The wheat plant was found to contain about one twentieth as much calcium and more than eight times as much silicon as the cotton plant. Wheat may be considered a silicon-accumulator plant. The chemical composition of the cotton plant is more closely correlated with the ion concentration, as expressed in the percentage of the ions in the cation exchange complex of soils, than is the composition of the wheat plant. Available data on chemical composition suggest that the wheat plant may be far more selective in the nutrients absorbed than is the cotton plant.

Investigations on Cecil sandy loam concerning the quantity of exchangeable cations, yield, and composition of cotton plants showed that there is no close relationship between concentration of cations in the soil complex and chemical composition of the cotton plant. The data available suggest that the relative strength of ions may be a much more significant factor in determining absorption and utilization of nutrients than is the concentration of ions in the nutrient media.

Data from a study on Orangeburg fine sandy loam and Norfolk fine sandy loam were very similar to findings on Cecil sandy loam, with the exception of the

higher sodium content of the plants grown on the Orangeburg and Norfolk soils. The chemical data show a wide variation in composition of the straw and kernels of wheat. The yield data suggest that growth of wheat is favored by a relatively large quantity of exchangeable calcium in the soil, but that large amounts of calcium are not absorbed by wheat plants. The sodium content of the straw is more than three times that of potassium. The wheat straw seems to accumulate sodium and silicon selectively, and the seed accumulates magnesium, phosphorus, and nitrogen selectively. As compared with the straw, the wheat seed apparently selectively excludes sodium, calcium, chlorine, and silicon.

The phylogenetic characteristics for protecting certain plants from excessive concentration of nutrient ions in the soil solution may result in a deficiency of such a nutrient as calcium in many humid-region soils relatively low in exchangeable calcium.

The selective exclusion of calcium from seeds, tubers, roots, fruits, and other reproductive tissue may significantly affect the structure, firmness, and keeping qualities of fruits, roots, and tubers grown on humid-climate soils. It has been noted that use of calcium salts in the processing of fruits has improved the firmness and physical appearance of the products. In many of our food-processing operations it may become desirable to add calcium to fruit products, particularly where ontogenetic requirements result in a strong selective exclusion of calcium.

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## AVAILABLE CALCIUM SUPPLY IN POORLY BUFFERED SOILS

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Because of their coarse texture and low content of organic matter, the soils of the Coastal Plain area of Southeastern United States probably are the most poorly buffered of the entire country. Since the Coastal Plain area of North Carolina is representative of these soils and more information is available on this area, this discussion, is centered around that area. In considering available calcium in the soils, three questions logically arise: What was the native supply? What is the present supply? What has happened in the interim?

### WHAT WAS THE NATIVE SUPPLY OF CALCIUM?

The present material of the Coastal Plain soils, in the main, according to Bennett (3, p. 68), was derived from the Piedmont, the Greater Appalachian, the Limestone Valleys, and the Uplands of the Great Plain regions. In North Carolina, the Coastal Plain soils were formed largely from the Piedmont and Blue Ridge Mountain material. The parent materials of the Piedmont and Blue Ridge Mountains are fairly similar and in many respects are somewhat complex, including crystalline igneous rocks such as granite, diorite, and gabbro; sedimentary rocks such as gneiss, schist, slate, and quartzite; and sandstone and shale.

The calcium content of Cecil soil, a predominating soil of the Piedmont area, varies tremendously, but usually ranges from a trace up to 0.34 per cent as total CaO in the A horizon (7). By way of comparison, the predominant soil of the Coastal Plain area is very probably Norfolk. No complete analyses are available on virgin soil of this series, but on the cultivated soil the calcium varies from 0.06 per cent to 0.61 per cent as CaO. The higher calcium content was very probably brought about by application of calcium in the form of lime.

The amount of calcium in the parent material and originally in the resulting soils, however, is of academic interest only, since there is little or no relationship between the original content and the present content of a Coastal Plain soil laid down in water and, since then, highly weathered and finally cropped for many years.

### WHAT IS THE PRESENT SUPPLY OF CALCIUM?

There is not much detailed information on the available calcium supply in the Coastal Plain soils. The Soil Testing Laboratory in North Carolina, however, has tested well over 100,000 samples of soil during the last 7 years. Though these data are perhaps not sufficiently detailed for the research worker, the results from such a large number of samples do seem to supply a practical answer to the question of the present supply.

Recently a survey was made of 1 year's results on these soil tests (11). Table 1 shows the pertinent data from the A horizon of samples tested from the Upper and the Lower Coastal Plain region, from the Sandhill area of the Coastal Plain, and from Ashe County, one of the better mountain counties.



In the Upper Coastal Plain region, 48 per cent of the soils were low in calcium and 7 per cent were very low. This means that more than 50 per cent of the soils contained 600 pounds or less of ground limestone per acre in available form in the A horizon.

TABLE 1  
*Results of soil tests in North Carolina*

	CLASSIFICATION OF SOIL SAMPLES			
	Upper Coastal Plain region (1,001 soils)	Lower Coastal Plain region (1,800 soils)	Sandhill area (233 soils)	Ashe County (689 soils)
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
pH				
Below 5.0.....	10	22	17	8
5.0-5.5.....	44	48	41	49
5.6-5.9.....	26	19	27	29
6.0-6.8.....	18	9	15	12
Above 6.8.....	1	2	1	1
Calcium*				
Very low.....	7	5	13	
Low.....	48	43	47	19
Medium.....	39	45	33	68
High.....	5	7	7	12
Magnesium*				
Very low.....	5	6	13	
Low.....	30	34	27	26
Medium.....	61	55	52	70
High.....	4	5	8	4
Organic matter				
Below 1.00%.....	45	19	38	2
1.00-3.50%.....	49	70	57	84
Above 3.50%.....	5	12	6	14

\* Approximate contents of calcium as carbonate and of magnesium as oxides, in pounds per acre in the A horizon, are as follows:

	Calcium	Magnesium
Very low.....	200	40
Low.....	600	60
Medium.....	1500	120
High.....	3500	320
Very high.....	5000*	400*

The Lower Coastal Plain region presents much the same picture. The soils of this area are near the coast, are less well drained, and generally contain more organic matter. They have, consequently, a higher exchange capacity and, as a group, have retained a little more calcium. Natively, the soils from the Sandhill area have the lowest exchange capacity of any group in the state, because of their coarse texture and low organic matter content in both the A and B horizons.

The organic matter picture on this area now, however, compares favorably with that on the Upper Coastal Plain area. This is likely because more effort is being made to maintain organic matter in the Sandhill area by increased use of soil-building crops in conjunction with peach and berry culture.

The results from Ashe County are presented in table 1 by way of contrast. The pH distribution compares fairly well with that of the Coastal Plain soils; but the calcium content is an entirely different picture. Sixty-eight per cent of the soils in this county contain medium quantities of calcium, or approximately 1,500 pounds of ground limestone to the acre, compared with only 39 per cent

TABLE 2

*Base-exchange capacity, base saturation, and pH of several soil types in the Coastal Plain area*

SOIL TYPE	HORIZON		BASE- EXCHANGE CAPACITY	pH AND DEGREE OF Ca-SATURATION				
				Natural soil		Satura- tion 25%	Satura- tion 50%	Satura- tion 75%
				Satura- tion	pH	pH	pH	pH
		<i>inches</i>	<i>m.e.</i>	<i>per cent</i>				
Norfolk fine sandy loam....	A <sub>1</sub>	0-6	5.34	13	5.0	5.45	6.20	6.98
Ruston sandy loam.....	A <sub>1</sub>	0-6	2.30	15	4.9	5.70	6.75	7.24
Okeene fine sandy loam....	A	0-6	4.30	7	4.8	5.58	6.20	6.85
Marboro fine sandy loam....	A	0-6	4.40	18	4.7	5.45	6.40	6.90

TABLE 3

*Some chemical characteristics of several productive Norfolk soils*

TEXTURE	CROP DESCRIPTION	pH	EXCHANGE CAPACITY	EXCHANGE- ABLE CALCIUM	ORGANIC MATTER CONTENT
			<i>m.e.</i>	<i>m.e.</i>	<i>per cent</i>
1. Sandy loam.....	Excellent alfalfa 6 years old	5.3	6.3	2.42	1.36
2. Sandy loam.....	Good alfalfa 4 years old	5.6	6.5	3.94	1.60
3. Sandy loam.....	Excellent corn	5.5	3.0	0.51	58
4. Fine sandy loam....	Good cotton and peanuts in rotation	5.15	3.07	1.36	1.28

in the Upper Coastal Plain area. Of course, the texture is much finer and the organic matter is much higher in the mountain soils than in the Coastal Plain soils, and consequently, the exchange capacity is considerably higher.

A recapitulation of the Coastal Plain soils from the data in table 1 shows that more than 50 per cent fall in the groups having a pH of 5.5 or less. This means that, in terms of degree of calcium saturation, more than 50 per cent of these soils are less than 25 per cent saturated. Data in table 2, from some work by Mehlich (8), illustrate this more fully.

This low calcium supply is by no means so serious as would appear. For example, table 3 shows data on samples of a Norfolk soil collected from four differ-

ent areas and gives a description of crop performance. Sample 1 has an excellent growth of alfalfa now in its sixth year, and yielded 3 tons of hay this year by August 25. This soil is a sandy loam to a depth of 26 inches before clay is reached. Sample 2 is somewhat similar, in that good alfalfa has been grown here 4 years and growth is still very good. Sample 3 has an excellent corn crop on it. This soil is a sandy loam to a depth of about 30 inches before clay is reached. Sample 4 is from a research plot used for cotton and peanut rotation, both giving good yields. The cotton produced a bale to the acre and the peanuts 1,500-1,800 pounds of nuts. In none of these samples did the calcium content exceed 3.9 m.e. Bayer (2), working with Missouri soils, found that a good soil had 18.6 m.e. of calcium and a poor soil had only 5.4 m.e. of calcium, or more than the highest found in the Norfolk soils.

#### WHAT HAS HAPPENED IN THE INTERIM?

According to Pierre (13), the Corn Belt used about 10,000,000 tons of lime, or 55 per cent of all lime used in the United States, in 1944. Truog (15) reported that about ten times as much lime was used in 1944 as was used 8 years earlier. In this connection, it is of interest to note that since Edmund Ruffin (14, p. 53), as shown by Craven (5, pp. 53-55), obtained such phenomenal results from the use of marl nearly 100 years ago on his Marine Terrace soil of the Pannunkey River Valley in Hanover County, Virginia, there has been considerable interest in liming Coastal Plain soils. Certainly, during the last 20 years, a rather concerted effort has been made to stimulate use of lime. Despite all efforts, however, only about 83 pounds of  $\text{CaCO}_3$ -equivalent was used per acre of cultivated land and open pasture in North Carolina in 1946.

Why is not more lime used? Admittedly, more lime could and should be used in North Carolina, if it were used wisely. However, there are some valid reasons why such small amounts are used in this area. Many of the crops grown, such as Irish potatoes and tobacco, have a relatively low lime requirement, as compared to cotton and legumes. There are also some physiological as well as pathological reasons to justify the practice. First, the exchange capacity of the average soil of this area is low, probably not exceeding 4.0 m.e. Second, the soils of the Coastal Plain are largely of the organic and the kalonitic or 1:1 mineral lattice type of colloid. From both of these colloid types, the calcium was found to be readily available, as shown by Mehlich and Colwell (9). These factors contribute very effectively to use by growing plants of a proportionally large part of the calcium present. With a low exchange capacity, relatively small amounts of calcium are required to effect the desired degree of saturation. The degree of saturation required for most general crops was found to be between 40 and 60 per cent for soils of the kalonitic type and between 25 and 40 per cent for soils of the organic type. Crops having an exceptionally high calcium requirement are benefited by a higher degree of calcium saturation.

Another reason why some farmers hesitate to use larger amounts of lime is fear of so-called overliming injury. Ruffin, in his writings, referred to the fact that

excessive use of marl reduced yields of crops. Problems of this type are occurring more and more frequently year by year.

Overliming is known to reduce the availability of potassium, as shown by McIntire and Shaw (6). It is likewise known to reduce the availability of boron, manganese, and iron, as shown by Albert (1), Bennett (4), Midgley (10), Naftel (12), Willis (16), and others. Supplying potassium and these trace elements may be expected to reduce injury of this type. Definite recommendations are not yet always possible. More information on the soil factors affecting overliming injury is greatly needed.

#### SUMMARY

The Coastal Plain soils of North Carolina are relatively coarse-textured and low in organic matter and therefore are poorly buffered. In this area very small amounts of lime are used and, indeed, relatively small amounts are needed. There are a number of reasons why such small amounts of lime are needed, namely:

The cation-exchange capacity of the average soil will probably not exceed 4.0.

When the total exchange capacity of the soil is that low, only small amounts of lime are needed to effect the desired degree of saturation.

The colloidal complex of these soils is largely of the organic and the kaolinitic or 1:1 mineral lattice type colloid.

The calcium from the organic and the kaolinitic type of colloid is relatively easily available for optimum growth of plants.

The overliming problem is annually increasing in severity. This adds to the relative complexity of liming sandy soils.

In view of the foregoing facts, there is perhaps no important soil area in the United States which uses lime so efficient as the Coastal Plain soils of the Southeast.

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## USE OF SOLUBLE SOURCES OF CALCIUM IN PLANT GROWTH<sup>1</sup>

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The poor growth associated with acid soils and its improvement by applications of liming materials have been the subject of extensive investigations. It is well recognized that calcium plays an important part in this phenomenon. Many comparisons have been made between the use of lime and the use of soluble sources of calcium on soils low in calcium, but most of them involve comparisons on soils that are strongly acid and with relatively high exchange capacities. There are comparatively few reports on the effects of adding soluble calcium salts to soils that are only moderately acid and that have low exchange capacities, and hence, low exchangeable calcium levels. In the cases so reported the soils have been only partly characterized.

Many of the old long-term experiments included comparisons of calcium carbonate with calcium sulfate on acid soils. Typical of the results of such experiments are those reported by the Indiana (1), Ohio (12), and Pennsylvania (11) Experiment Stations. Lime improved the growth of plants and greatly increased yields over the years, but calcium sulfate was relatively ineffective. Gedroiz (7) also reported upon the importance of lime and the relative ineffectiveness of calcium sulfate and stressed the effects of soluble aluminum in acid soils. These experiments were conducted on rather strongly acid soils the colloidal complexes of which were largely saturated with hydrogen.

In more recent years, several workers have postulated that the supplying of nutrient calcium is one of the chief reasons for liming. Plant physiology textbooks emphasize the importance of the element calcium as a plant nutrient. Numerous physiological roles have been ascribed to calcium, though some of these are little understood. Calcium has an influence on the translocation of carbohydrates and proteins and on their storage during seed formation. Calcium is a component of plant structure and compounds, and it influences the physiological availability of other ions, such as nitrogen. General responses of plants to calcium in water and sand cultures have been demonstrated repeatedly.

Truog (13) in an early study of soil acidity in its relation to plant growth suggested that the reason calcium sulfate did not prove beneficial on acid soils was that the plant needed calcium, not so much as a plant nutrient, but to neutralize the acids formed within the plant. He concluded, therefore, that to be of value calcium must be present in soils in the carbonate or bicarbonate form. Hoagland (8) does not exactly agree with this concept relative to the assimilation of calcium and the role it plays in the plant. He has pointed out that oxalic acid is synthesized in the plant. When nutrient solutions are varied in composition so as to bring about increasing calcium absorption, increasing concentrations of oxalic acid appear in the plant.

<sup>1</sup> Contribution from the North Carolina Agricultural Experiment Station. Published with the approval of the director as Paper No. 270 of the journal series.

Work on the role of calcium in plant nutrition has been carried out by Albrecht (2, 3). He emphasized the important role played by calcium and distinguished between the effects of acid reaction and the direct nutritive effect of calcium. He presented data to support his contention that "calcium occupying so large a portion of the adsorbed and exchangeable store of cations on the clay becomes plant nutrient number one in importance." In many of his illustrations of the importance of calcium, the pH was maintained constant, and increasing amounts of calcium were supplied. These usually involved the addition of increasing amounts of clay, however, and there has been some question as to whether the better growth was due entirely to the level of calcium. In the few comparisons Albrecht made between calcium in the adsorbed form and soluble sources of calcium, clay on which calcium was adsorbed was superior in that it supported growth over a wider range of calcium offered the plant than was possible by aqueous solution. He suggested that compounds of calcium other than carbonates (compounds that do not neutralize soil acidity) could be used in place of lime. Yet most of his experiments were actually with calcium adsorbed on the clay particle. His evidence points to the importance of degree of calcium saturation in relation to calcium availability.

Albrecht contended that the hydrogen-ion attached to the colloidal fraction was not in itself injurious. If the degree of calcium saturation increased with a corresponding increase in both pH and calcium level, he assumed that the increasing calcium level was responsible for better growth. If the amount of clay was varied so as to give the same amount of calcium at varying degrees of calcium saturation, he assumed that it was the greater release of calcium from the colloid at higher degrees of saturation that was responsible for better growth, rather than the increasing pH.

Gedroiz had suggested earlier (7) that two factors prevented plant growth on a soil fully saturated with hydrogen ion and given no calcium carbonate: the absence of available calcium, and the acid reaction. He pointed to the injurious effects of the acid reaction, since introduction of calcium sulfate in place of calcium carbonate in a hydrogen-saturated soil failed to produce good growth. Albrecht suggested that in such cases the sulfuric acid formed from the introduction of calcium sulfate into a hydrogen-saturated soil could be the cause of plant growth failure. In other words, the adsorbed hydrogen ion in an acid soil is not necessarily the injurious factor. This possibility of strong acid production exists, of course, when most soluble sources of calcium are applied on acid soils. Yet Arnon and Johnson (4), working with nutrient solutions, found that at a pH value lower than those usually encountered in acid soils, acidity, as such, was not injurious to plant growth. Regardless of the exact factor responsible for poor growth at low soil reactions, the evidence is fairly conclusive that application of soluble sources of calcium at low pH values would not be generally satisfactory.

Fried and Peech (6) recently reviewed the literature on this subject and presented comparisons of lime and gypsum on the growth and composition of several crops. Gypsum produced much lower yields of crops yet resulted in a much greater concentration of calcium in the soil solution. These workers, after con-

sidering the subject from various angles, concluded that the reasons for the poorer growth with gypsum and the inability of the plant to absorb calcium from the relatively soluble gypsum are quite obscure.

Perhaps we have been failing to characterize our soils sufficiently in such cases. It is recognized that in soils with colloid of the 2:1 type, a higher degree of calcium saturation and a higher calcium level are required for good growth and for comparable plant absorption of calcium than on soils of the 1:1 type of colloid. The suggestion has been made that competition with the hydrogen ion is much more pronounced in soils of the 2:1 colloid type than in soils of the 1:1 type. It is conceivable, then, that with soils of the 1:1 type, response to calcium and increased calcium uptake would occur at 20 per cent calcium saturation, whereas no such response would occur with soils of the 2:1 type colloid at the same degree of saturation. Such postulations could be made on the basis of some of Mattson and of Wiklander's work, although this remains to be explored fully.

In general, we may expect beneficial results from the use of soluble sources of calcium under three conditions: (a) in soils of very low exchange capacity where the possibilities of building up levels of exchangeable calcium are limited; (b) in soils of moderate acidity where it is desirable to keep the soil reaction fairly low and yet supply calcium for plant growth; (c) in soils of either low or high exchange capacity where the crops have a high calcium requirement at certain stages of growth, or where it is necessary to supply calcium to certain soil zones.

The properties of soils of low exchange capacity and the problems involved in liming them are discussed by Miles in another article in this journal. Some of the difficulties involved in building up the level of calcium in such soils will be illustrated later.

The second situation is well illustrated in experiments with tobacco conducted by McMurtrey (9). Tobacco is a crop with reasonably high calcium requirements, but in its culture it is often considered desirable to keep the soil reaction down. On some soils in Maryland the native supply of calcium was found to be inadequate for normal growth. Calcium supplied in the form of nitrate, sulfate, or phosphate was as effective as the carbonate in producing normal growth of tobacco. The symptoms of calcium deficiency, as described by McMurtrey, are distinct from the symptoms associated with acid soil reactions, which might be the results of toxicity due to excessive manganese, aluminum, or hydrogen. Hence they are useful in establishing situations where soluble calcium salts would be beneficial.

The third situation, where a high concentration of soluble calcium is essential in certain soil zones, is illustrated in recent work with peanuts in North Carolina. For years calcium sulfate has been applied to peanuts by farmers. Lime has also been used, and experimental comparisons of the two were frequently difficult to interpret. There appeared to be little correlation between soil pH and response of peanuts to lime or gypsum. It was then established that peanuts require calcium in the soil area in which the peanut fruit is produced (5). That it was calcium and not the anion associated with it that was required was verified by experiments designed to compare calcium and other cations associated with various anions. This is illustrated in figure 1. This discovery explained why

applications of calcium sulfate to the foliage were superior to applications of dolomitic limestone in the row in experiments comparing the two practices. The difference in quality of peanuts with these two practices is shown in figure 2,

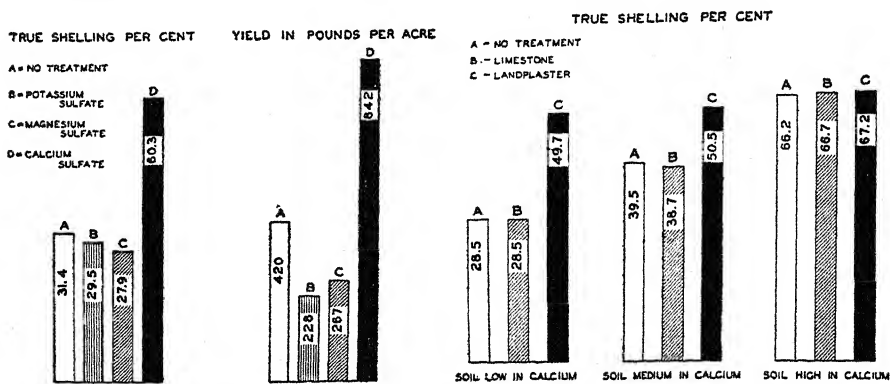


FIG. 1

FIG. 2

FIG. 1. EFFECTIVENESS OF CALCIUM SULFATE IN INCREASING YIELD AND SHELLING PERCENTAGE OF PEANUTS, IN CONTRAST WITH INEFFECTIVENESS OF CATIONS OTHER THAN CALCIUM ASSOCIATED WITH SULFATE

FIG. 2. INEFFECTIVENESS OF DOLOMITIC LIMESTONE PLACED IN THE ROW AT PLANTING, IN CONTRAST WITH EFFECTIVENESS OF LANDPLASTER (CALCIUM SULFATE) PLACED ON TOP OF THE ROW AT PEGGING TIME, INCREASING SHELLING PERCENTAGE OF PEANUTS

Note the effect of level of soil calcium (5)

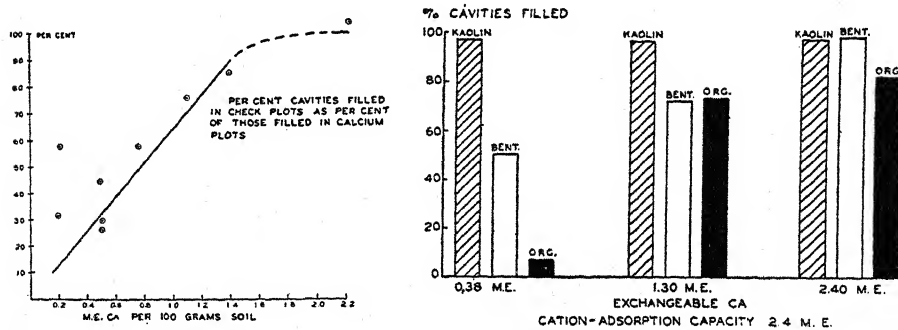


FIG. 3

FIG. 4

FIG. 3. RELATIONSHIP BETWEEN SOIL CALCIUM LEVEL AND PERCENTAGE FILL OF FRUIT IN PEANUTS GROWN ON SIMILAR SOIL TYPES (5)

FIG. 4. CALCIUM REQUIREMENTS OF PEANUTS PRODUCED IN MEDIA IN WHICH THE CALCIUM IS ADSORBED ON THE KAOLINITIC MINERAL TYPE COLLOID AND ON THE BENTONITIC AND ORGANIC TYPES (10)

which also brings out the fact that there is a relationship between the soil calcium level and the need for calcium sulfate. The results led to efforts to apply chemical tests to determine when the soil needed additional calcium. In a series of tests in a single area where the soils were of similar types, a close relationship was found between exchangeable calcium and percentage fill of peanut fruit (fig. 3).

Simple tests of calcium level, however, provided rather disappointing correlations with calcium needs when these tests were applied to other areas of different soil types. Soils with higher exchangeable calcium levels frequently showed better response to added calcium than did soils of lower calcium levels. Then it was observed that information was needed not only on the level of exchangeable calcium but on the type of colloid with which it was associated (10). This is brought out in figure 4, which shows that a lower level of calcium is sufficient if peanuts are produced in a soil with colloid predominantly of the 1:1 mineral type. Apparently these differences may be due to a greater ease of release of calcium from

TABLE 1  
*Calcium in 1:1 colloid:H<sub>2</sub>O solution at the end of the growing period of peanuts*

COLLOID	CATION- ADSORPTION CAPACITY	EXCHANGEABLE Ca		Ca IN SOLUTION	FRUIT QUAL- ITY (CAVITIES FILLED)
	<i>m.e.</i>	<i>m.e.</i>	<i>per cent</i>	<i>m.e.</i>	<i>per cent</i>
Kaolinite.....	1.2	0.26	22	.045	83
Organic.....	1.2	0.26	22	.015	32
Organic.....	12.0	2.76	23	.043	85

TABLE 2  
*Effect of lime and gypsum on peanut quality*

TREATMENT*	Ca ADDED	Ca IN UPPER 3 INCHES		PEANUT CAVI- TIES FILLED (1946)
		1st year	2nd year	
	<i>m.e./100 gm.</i>	<i>m.e./100 gm.†</i>		<i>per cent</i>
None.....	0	0.31	0.29	12.4
1200 lbs. dolomitic lime broadcast.....	0.66	0.82	0.60	32.2
2400 lbs. dolomitic lime broadcast.....	1.32	1.20	0.86	45.3
620 lbs. dolomitic lime topdressed.....	0.33	....	....	64.0
640 lbs. gypsum topdressed.....	0.33	....	1.32	86.8

\* Lime broadcast 17 months previous and topdress applications made 2½ months previous to sampling on August 20, 1946.

† Ca in soil during fruit development, first year (1945) 5 months after liming, and second year (August 20, 1946) 17 months after liming.

the 1:1 type of mineral colloid. This is suggested by data in table 1, taken from work of Mehlich and Reed (10), which show that in simple water solution more calcium is released by the 1:1 type of colloid than by the organic type.

Whether lime or a soluble source of calcium should be used would depend on whether it is possible to supply calcium in a soluble form more cheaply and easily than lime, and whether it is more effective in this form. Two factors should be recognized in this connection. In the first place, broadcast applications of lime on soils of low exchange capacity may be soon dissipated. This is illustrated by data from a 2-year experiment in which lime was broadcast the first year and compared with calcium sulfate and lime applications made locally each year. Data in table 2 show the difficulties involved in building up a level of exchange-



able calcium in a soil of low exchange capacity (2.40 m.e. per 100 gm.). The data show also that the percentage fill is greatest when calcium sulfate is applied on top of the row. The level of calcium in the area in which the peanut fruit forms is greatest here too, even though only half as much calcium was added in 2 years as with the broadcast applications of dolomitic lime. In the second place, it is quite possible that it may be necessary to apply greater amounts of calcium sulfate on soils relatively high in organic matter because of the effect of type of colloid. This, of course, is true of lime also and is illustrated in figure 5. Peanut fruits were produced in a soil high in organic matter upon which two levels of exchangeable calcium had been established. Calcium sulfate (plaster) differentials were superimposed upon the calcium levels. If peanuts are produced on a

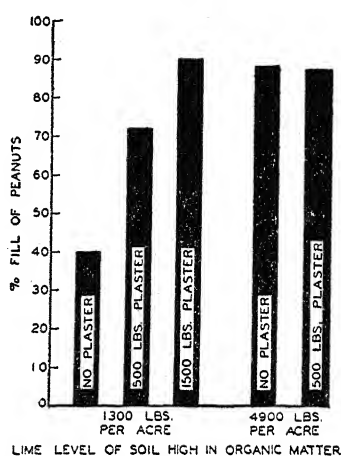


FIG. 5. CALCIUM REQUIREMENTS FOR SATISFACTORY FILL OF PEANUTS ON SOIL HIGH IN ORGANIC MATTER

Either higher lime levels or larger applications of calcium sulfate are necessary on such soils than on soils lower in organic matter

soil high in organic matter, either a high lime level must be established by liberal use of lime, or a large application of calcium sulfate is necessary.

These data illustrate the fact that soluble sources of calcium may have a definite place with certain crops. Their general use has been of very limited value on acid soils of high exchange capacity that are low in exchangeable calcium and high in exchangeable hydrogen. On such soils the response to lime involves many contributing factors in addition to the supply of calcium.

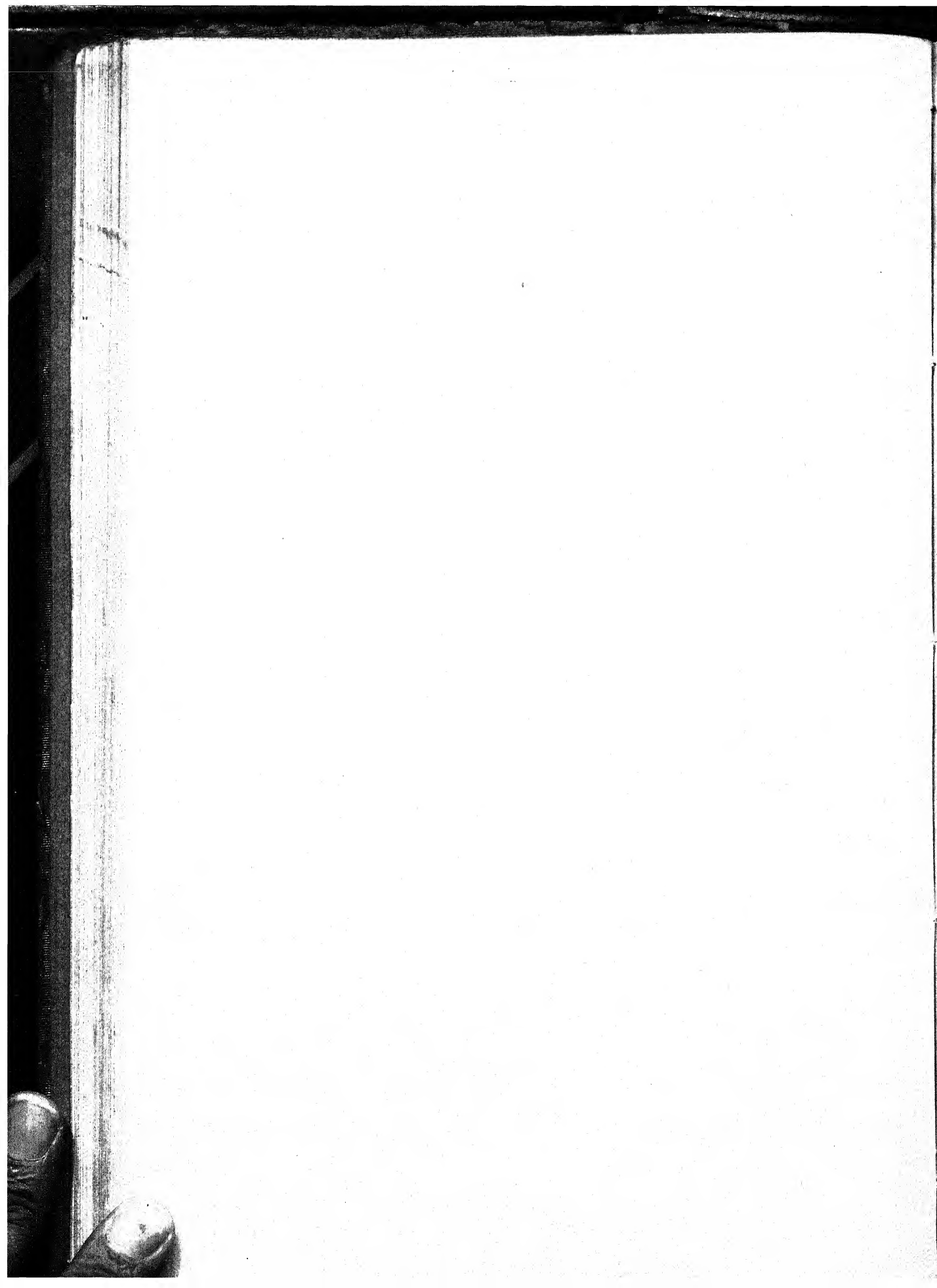
#### SUMMARY

Results of various investigations on additions of soluble calcium, particularly as compared with lime applications, are given. Data are presented from recent experiments involving the use of calcium sulfate on peanuts. Peanuts require a high level of calcium in the soil area in which the fruit is formed. The effect of the type of soil colloid on response to calcium applications is emphasized. Com-

parisons are given between the use of lime and calcium sulfate as sources of calcium for peanuts. Available data indicate that soluble sources of calcium may have a definite place with certain crops. Their general use has been of very limited value on acid soils of high exchange capacity that are high in exchangeable hydrogen.

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## REVIEW OF THE RELATION OF CALCIUM TO AVAILABILITY AND ABSORPTION OF CERTAIN TRACE ELEMENTS BY PLANTS<sup>1</sup>

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The calcium content of the soil has long been known to influence availability and absorption of other nutrient ions by plants. To a major degree, this effect of calcium upon solubility of other soil-borne nutrients depends on the attendant soil reaction. As the soil reaction approaches and exceeds neutrality, calcium ions may eliminate certain nutrient anions from the soil solution through precipitation as relatively insoluble calcium salts. Under similar conditions of soil reactions several essential cations are rendered insoluble through reactions that may, or may not, directly involve the calcium ion.

From the standpoint of the plant, calcium ions play a highly important physiological role in regulating the membrane permeability of absorptive tissues to such ions as sodium, potassium, and magnesium. Little is known, however, regarding the effect of this function of calcium upon the entrance of the minor nutrients into plants.

Calcium is an essential element in all plant tissues, and a deficiency of this ion soon disrupts the utilization of all other nutrient ions. The important consideration in plant nutrition is the adequacy of the supply of each nutrient in relation to the rate of growth of the plant at any given time and in relation to the concentration of other nutrients that may influence its absorption. Obviously, as the rate of growth of the plant is increased by favorable environmental conditions, the demand for nutrients is likewise increased. In certain stages of growth, the demand for specific nutrients may increase. A fruiting apple tree, for example, will require more boron than a nonfruiting one.

The calcium ion, or the reaction of the soil, is believed to influence availability of the four minor nutrients considered in this paper as indicated in the separate discussions of each nutrient.

### BORON

It is generally agreed that overliming a soil will often induce boron deficiency. Several theories have been advanced as to the means by which the action of lime reduces the boron content of the soil solution so that it is unable to supply this nutrient to plants in required amounts. The question at once arises as to what we mean by the term "overliming." The acid soils of the eastern seaboard are low in organic matter and respond readily to liming, but the increased plant growth makes additional demands for an increased supply of all other plant nutrients. Here we are dealing with a substitution of limiting factors. Elimination of one deficiency, or unfavorable soil condition, chiefly responsible for retardation of plant growth in a particular soil must inevitably result in a de-

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iciency of a second limited nutrient, or the appearance of another unfavorable soil condition.

It is believed that most of the boron deficiency occurring on the light acid soils of the East falls into the above category. Liming these soils will often produce boron deficiency at a pH of 6.0 or below. These soils simply do not contain sufficient boron for optimum plant growth. That raising the pH of these soils does not affect the water-soluble boron content has been demonstrated by Reeve, Prince, and Bear (14) and by Purvis and Hanna (13). Obviously, we are not dealing here with true overliming, although liming did result in the boron deficiency.

If we define "overliming" as the use of lime to such an extent that its benefits are surpassed by factors that act adversely upon availability of other plant nutrients, normally present in sufficient amounts in the soil solution, we have an entirely different problem from the previous one. Many workers have shown that specific soils, normally containing ample available boron for plant growth, become deficient in this nutrient when limed to pH 7.0 and above. Sometimes these soils have a capacity to fix applied boron so rapidly that soil treatments are futile and the nutrient must be applied to the leaves in a spray. The mechanism of this fixation has been the subject of much study. Naftel (12) attributes the fixation to increased microbial activity promoted by lime. Other workers (5) have presented evidence that the growth of certain fungi is stimulated by the addition of borax to both acid and limed soils. Midgley and Dunklee (11) concluded that the fixation of boron in overlimed soils is a function of the soil organic matter, which assumes a high fixing power for boron once it is activated by lime.

The work of Brenchley and Warrington (1), Marsh and Shive (10), Jones and Scarseth (7), and others has fairly well established the existence of a functional relationship within the plant between boron and calcium. These nutrients must be available in proper balance for normal growth. A low intake of either causes the plant to require less of the other. Likewise, a high intake of one increases the requirement of the plant for the other. Thus we must add another factor to those influencing boron deficiency on overlimed soils. Plants growing on these soils have a higher boron requirement for each unit of growth due to an increased calcium intake.

#### COPPER

Bryan (2) found copper deficiency in citrus more prevalent on acid soils than on neutral soils in Florida, and Harmer (6) reported that the muck soils of Michigan gave a greater response to copper when the pH was below 6.0 than when the soil reaction was above this figure, although a few crops responded to added copper when the soil pH exceeded 7.0. Australian workers (15, 18) have reported response to copper applications on very acid mucks as well as on calcareous soils. Williams (19) obtained plant injury from an application of 50 pounds of copper sulfate per acre on an unlimed North Carolina soil, and no effect from copper, applied at the same rate, when the soil was limed with 2 tons of limestone per



acre. When an application of 6 tons of limestone per acre was made, however, a decided response to copper was obtained.

The above data indicate that available copper becomes fixed in soils limed in excess of neutrality and is lost by leaching in more acid soils.

#### MANGANESE

The first widespread appearance of manganese deficiency under field conditions to be reported in this country occurred in Rhode Island, one of the first states to undertake an extensive liming program. In a series of papers appearing over a period of years, McLean and Gilbert (9) established the cause as lime-induced manganese deficiency and demonstrated that it could be corrected by soil amendment with applied manganese, or by spraying weak manganese solutions directly to the foliage. The disturbance occurred on soils ranging in pH from 6.2 to 6.9. With increasing use of lime the disturbance became prevalent in other sections of this country and throughout the world, having been reported from Europe as early as 1909. During the last two decades numerous papers on the subject have appeared. Recent papers of Leeper (8) and Sherman (16) include extensive reviews of the literature.

From the mass of available published information the following statements regarding the effect of lime upon Mn availability seem to be warranted:

1. Only the manganous, or reduced, form of manganese is immediately available to plants.
2. The oxidation-reduction status of the soil will determine availability of soil manganese.
3. Liming acid soils reverses the oxidation-reduction equilibrium and results in fixation of available manganese.
4. Disagreement exists as to whether this oxidation is brought about by soil bacteria or by nonbiological means.
5. Plant recovery can be induced by soil treatment with soluble manganese salts, by acidifying the soil, by establishing reduction processes in the soil as by flooding, and by spraying weak manganese solutions directly on the foliage.
6. Soil tests for manganese sufficiency must include determinations of the easily reducible manganese (extractable with neutral normal ammonium acetate containing 0.2 per cent quinhydrone) as well as the exchangeable manganese. Sherman and Harmer (17) set 3 p.p.m. of exchangeable supplemented by 100 p.p.m. of easily reducible manganese as the minimum content necessary for normal plant growth on alkaline soils.

During the last 2 years numerous instances of lime-induced manganese deficiency in several leafy crops have occurred in New Jersey. As in the earlier case in Rhode Island, this condition developed as an aftermath of an enthusiastic liming program. In all cases investigated, the soil reaction was 6.5 or above but seldom exceeding neutrality. The condition was readily recognized from previous experience with it in Florida and Virginia. In several instances, plants responded to applied manganese sulfate and to weak manganese sprays. As often occurs, crops sometimes recovered without treatment.

This question of why manganese deficiency will often appear temporarily in a field and correct itself without treatment, and why the deficiency does not al-

ways occur on overlimed soils has long been of interest to many of us. It is possible that the explanation lies in the long-known fact that the soil reaction is not constant even within the surface soil. Determinations of soil pH are normally run on composite samples, and the figure arrived at is an average one for the soil as a whole. Yet in most soils there are small pockets, or areas, where considerable deviations from this average figure are easily detected. Cells of soil, within an inch or so of one another, have been found to vary in reaction in excess of a full pH unit in fields that have not been limed for more than 5 years. In recently limed soils this variation will normally exceed 2 pH units. Figure 1 illustrates this point. The clod is roughly 6 inches in diameter. The pH determinations were made on aggregates of soil approximately  $\frac{1}{2}$  inch in diameter from locations as illustrated.

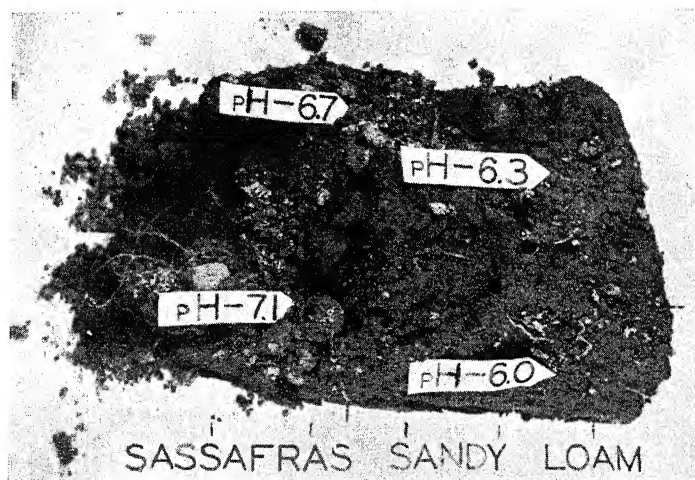


FIG. 1. VARIATIONS IN REACTION WITHIN A 6-INCH CLOD OF SOIL

That this condition is common, and not the exception, is indicated by the fact that it is more difficult to find a clod of soil that will not show a variation in reaction than to find one that will. Microdeterminations would undoubtedly show even greater variation. Such pockets of variable reaction may result from a number of factors, among which may be listed the practical impossibility of thoroughly incorporating liming materials into a soil, the oxidation of sulfur-containing minerals, and the production of acids in decomposition of organic materials.

It is suggested that as long as the number and size of such acid pockets are sufficient to supply the required manganese, and other nutrients that are fixed at higher reactions, plant deficiencies of these nutrients will not appear even on soils where the composite reaction exceeds neutrality. Such deficiencies will appear when these soil areas of variable reaction are eliminated or when the more acid pockets are raised in reaction to points in excess of approximately pH 6.5.

Such a condition can conceivably be brought about by brief periods of moisture saturation in overlimed soils where the reaction of the soil solution within the root zone of plants must approach uniformity as the hydroxyl ions of the preponderantly alkaline soil invade the local areas of greater acidity and neutralize them. So far as the plants are concerned, similar results would occur during extremely dry periods when the low moisture content of these acid areas would prevent the plants from obtaining sufficient nutrients from these limited sources.

#### ZINC

The relationship between zinc deficiency and soil reaction appears to be generally accepted. As early as 1917, Floyd (4) described physiological symptoms in citrus, produced as the result of overliming, that are now recognized as typical of zinc deficiency. Camp (3) in summarizing his own extensive work on the subject, as well as that of a number of other investigators, pointed out that "it seems reasonably well established that the availability of zinc declines as the pH of the soil rises, the critical point being somewhere between pH 5.5 and 6.5." This similarity to manganese availability should be noted.

#### SUMMARY

As the soil reaction approaches and exceeds neutrality, availability of boron, copper, manganese, and zinc decreases.

The calcium ion is not known to play a part in this fixation, except possibly in the case of boron.

A functional relationship between boron and calcium exists within the plant, and a high intake of one of these nutrients will increase the requirement of the plant for the other.

Soil microbes are believed to have an important part in oxidation of manganese and in fixation of boron.

The soil mass usually does not have a constant reaction but is honeycombed with small zones of varying pH. Since there is no single reaction at which all nutrients are equally available to plants, it is perhaps fortunate that the soil medium surrounding the roots of plants is usually variable in pH. When this medium becomes constant in reaction, deficiency symptoms of one or more plant nutrients are likely to occur.

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## CALCIUM CONTENT OF SOILS AND FERTILIZERS IN RELATION TO COMPOSITION AND NUTRITIVE VALUE OF PLANTS

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*Campbell Soup Company*

Calcium makes up approximately 40 per cent of the mineral elements of the human body. To maintain a positive calcium balance, a daily intake of 0.8 gm. of available calcium for a 150-pound man (12) and larger amounts for pregnant women and growing children (19) are recommended.

Records of a large number of soldiers on field rations that furnished adequate energy, an average of 3,740 calories daily, and allowed some free choice of food, showed a daily calcium intake of 1.2 gm. This ration provided fluid milk equivalent of 1.2 pounds daily, which furnished more than 70 per cent of the total calcium consumed. Vegetables, fruits, and cereal and grain products furnished only 0.21 gm. of calcium daily or 20 per cent of the total calcium intake. Green and leafy vegetables of good quality, though much lower in calcium than milk, are important as a source of calcium in the diet. The consumption of milk and the total energy in this army ration are far above the national average. A high calcium content of vegetables and fruits is necessary if the calcium intake is to be maintained at adequate levels for that portion of the population which has a low milk consumption.

Analyses of Coastal Plain soils (10) where large acreages of vegetables are grown for eastern markets show that over 35 per cent have a pH of 5.4 or below. These soils are principally sands or sandy loams developed from noncalcareous materials and have a low exchangeable calcium content. Vegetables from this area frequently show below average calcium content. The low fertility of these soils requires the use of large amounts of fertilizers to produce satisfactory crop yields. Analyses (16) show that these fertilizers contain about 14 per cent CaO. This added calcium, with that furnished in liming materials, has enabled growers who follow good soil management practices to produce foods having a calcium content equal to or above that of foods produced in regions where the natural calcium content of the soils is higher. A large portion of our population lives along the Atlantic Coast and in the Coastal Plain area. Although modern preserving methods and transportation permit foods to be shipped great distances, much of the vegetable produce consumed in eastern metropolitan areas is grown on Coastal Plain soils. It is therefore important that the produce grown here have a high calcium content if the calcium intake of this portion of the population is to maintain a positive calcium balance.

The minimum calcium requirement of most domestic animals has not been determined accurately, but it is variously reported (7, 17) as ranging from 0.2 to 0.7 per cent of the ration. The calcium content of grains is relatively low, and animals receiving no other feed may develop calcium deficiencies. Where rations provide a considerable quantity of legume hay from high-calcium soils, the chances of calcium's being deficient for animals is not great. Where the



available calcium in a soil becomes so low, however, that high-type legumes (alfalfa and clovers) can no longer be satisfactorily grown, and grasses or "acid-tolerant" legumes make up the bulk of the forage, then calcium intake of animals may drop below the adequate level (1).

#### EFFECT OF CALCIUM ON PLANT COMPOSITION

Summaries of the effect of liming materials or calcium-bearing fertilizers (2, 21, 23) show that the influence on the calcium content of plants is highly variable. In some cases the percentage of calcium in plants is increased where lime is applied. Other cases show no change. Some instances are reported, however, where plants grown on limed soils actually show a lower calcium content than those on unlimed soil. Frequently the addition of lime alone results in a greater effect on the percentage of protein, phosphorus, lignin, or silica than on the calcium content. This variation is shown in table 1 where addition of enough

TABLE 1  
*Effect of soil liming on calcium content of vegetables*

pH	CaCO <sub>3</sub> ADDED PER A.	CaO CONTENT*		
		Cabbage	Garden peas	Lima beans
	<i>lbs.</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
4.4	0	4.42	6.78	5.07
5.0	1,323	6.38	9.58	6.43
5.5	2,646	7.50	8.88	6.60
5.9	3,969	7.53	8.70	6.60
6.2	5,292	6.92	8.82	8.60
6.4	6,615	6.59	9.30	7.15
7.0	10,584	7.40	9.33	7.54

\* Dry-weight basis.

lime to a low-calcium soil (pH 4.4) to bring the pH to 5.0 and 5.5 gave an increase in the calcium content of cabbage and peas. Additional lime, however, resulted in no further increase in percentage calcium in these crops. In lima beans on the same soil the maximum calcium content was not reached until 5,292 pounds of lime per acre was added and the pH reached 6.2. These data illustrate why it is possible for several investigators working on the same soil type to draw different conclusions.

The composition of soybean hay grown on Putnam silt loam (table 2) too low in calcium and too acid (pH 5.4) to grow high-type legumes without liming, indicates that addition of limestone failed to increase the calcium content of the soybeans but produced a significant increase in the nitrogen and phosphorus content. The calcium content of the potash-deficient beans was the lowest for all hays despite the soil liming. This would indicate that plants deficient in one element may fail to absorb from the soil other nutrients that are present in abundance.

Soil fertility has been shown to have a pronounced effect on the composition of

tomatoes (11). Where soils are low in calcium and are acid or deficient in an essential nutrient, it is not likely that satisfactory yields or a product of desirable taste or appearance will be obtained. Raising the calcium content of the soil when other elements were deficient did not produce tomatoes of good quality. The data in table 3 show the changes in composition of tomato puree when calcium and magnesium limestone were added to an acid soil that received liberal quantities of other nutrients. Addition of the limestone produced a marked increase in available calcium, magnesium, and phosphorus and a great reduction in toxic aluminum and manganese in the soil. In this experiment liming increased the content of ascorbic acid and sugars, reduced the acidity, and improved the color of the puree. There was little effect on the calcium or magnesium content of the puree, though the manganese and copper contents were reduced. The high acid and low sugar content of the tomatoes from the unlimed soil made for a product of low quality.

TABLE 2  
*Relation of soil treatment to composition of soybeans*  
Putnam silt loam, pH 5.4

SOIL TREATMENT	SOYBEANS			
	Yield per acre	N Content	P content	Ca Content
	lbs.	per cent	per cent	per cent
None.....	2780	2.35	.217	1.31
150 lbs. 0-20-0.....	2500	2.15	.240	1.28
150 lbs. 0-20-10.....	3800	2.50	.232	1.35
150 lbs. 0-20-0* plus limestone.....	2940	2.78	.260	1.07
150 lbs. 0-20-10 plus limestone.....	3800	2.92	.262	1.28

\* Extreme potash deficiency.

#### EFFECT OF LIMING ON PROPERTIES OF GRAIN

Grains are relatively low in calcium (table 4), but when they are grown in rotation with legumes, application of lime increases nitrogen fixation, which may greatly influence the protein content. Analyses of some corn grain produced in Illinois (22) showed an increase in protein content of 40 per cent due to application of lime alone.

Lime applied in the legume rotation may affect the hardness of corn. It is evident from the data in table 5 that corn produced on soils supplying excessive nitrogen is harder than that produced on soils in which the nutrient supply is more nearly balanced. Where lime and sweet clover for a green manure are the only soil treatments, calcium and nitrogen are available in much greater quantities than are phosphorus and potash. When animals were given free choice of these grains, they invariably selected the softer corn or grain produced on soil having a more nearly balanced supply of nutrients. Regardless of animal choice, it is not unreasonable to assume that the addition of calcium to a soil, which alters the total protein content and hardness of grains, may change the propor-

TABLE 3

*Effect of limestone on soil nutrients and on composition of tomatoes grown on Sassafras sandy loam\**

SOIL TREATMENT	SOIL pH	SOIL ANALYSES AT HARVEST †					
		CaO	MgO	P <sub>2</sub> O <sub>5</sub>	K <sub>2</sub> O	Mn	Al
None.....	4.6	336	70	5	360	4.7	4.5
Calcium limestone.....	6.6	4200	170	60	360	0.8	1.6
Dolomitic limestone.....	6.2	1680	170	53	360	1.1	2.5

SOIL TREATMENT	YIELD OF TOMATOES	COMPOSITION OF TOMATO PUREE			
		Ascorbic acid	Sugars	Acids	Color‡
	gm.	p.p.m.	gm./l.	m.e./l.	
None.....	505	96	30.4	71	D
Calcium limestone.....	1211	161	37.2	50	C
Dolomitic limestone.....	1330	170	32.2	59	B

SOIL TREATMENT	ANALYSIS OF TOMATOES§						
	Ca	Mg	K	P	Fe	Mn	Cu
None.....	.80	.93	10.9	4.4	1.4	.92	.10
Calcium limestone.....	.95	.93	9.9	5.4	2.4	.37	.01
Dolomitic limestone.....	.55	.78	9.5	4.6	2.2	.22	.05

\* Grown in pots containing 95 pounds of soil and receiving liberal applications of 12-24-24 with minor elements.

† Soil extracted by Hester soil analytical method. Results expressed in pounds of nutrients per acre.

‡ Attractiveness of color designated alphabetically: A, Very Good; B, Good; etc.

§ In milliequivalents per 10 gm. dry weight.

TABLE 4

*Calcium content of grains\**

	NUMBER OF ANALYSES	Ca CONTENT		
		Maximum	Minimum	Mean
		per cent	per cent	per cent
Barley grain.....	170	.22	.07	.14
Corn grain.....	127	.045	.006	.015
Cotton seed.....	10	.31	.08	.15
Cowpea seed.....	2	.349	.242	.296
Oat grain.....	170	.19	.05	.10
Rye grain.....	10	.207	.043	.115
Soybean seed mature.....	9	.30	.19	.24
Wheat grain.....	290	.122	.005	.050

\* From Beeson (2).

tion of amino acids and other organic compounds formed that will influence the metabolism of animals.

#### LIMING AND THE VITAMIN CONTENT OF PLANTS

Comparatively little (15) has been done on the relation of soil fertility to vitamin content of plants, except for the influence of some minerals on the formation of ascorbic acid. Results of some workers (9, 11, 25) show an influence of some soil nutrients on vitamin C, whereas other investigators (13) have failed to find correlation.

TABLE 5

*Relative hardness of corn grain in 2-year rotation of corn, wheat, and sweet clover—with and without lime\**

SOIL TREATMENT	RELATIVE HARDNESS†
None.....	16.4
400 lbs. 0-10-10.....	15.8
Manure—8 tons on corn.....	18.0
400 lbs. 0-10-10 and manure—8 tons on corn.....	18.0
Lime and sweet clover (under).....	20.0
400 lbs. 0-10-10 and lime and sweet clover (under).....	15.5

\* Unlimed soil too acid and low in calcium to grow sweet clover.

† Relative force required to push a 15° point, 2 mm. in diameter, into the endosperm.

TABLE 6

*Effect of various nitrogen, manganese, and potash levels on ascorbic acid content of oats\**

NH <sub>4</sub> NO <sub>3</sub> UNITS	ASCORBIC ACID CONTENT OF OATS†							
	Low potassium				High potassium			
	0 MnSO <sub>4</sub>	1 unit MnSO <sub>4</sub>	2 units MnSO <sub>4</sub>	4 units MnSO <sub>4</sub>	0 MnSO <sub>4</sub>	1 unit MnSO <sub>4</sub>	2 units MnSO <sub>4</sub>	4 units MnSO <sub>4</sub>
0	158	162	187	222	128	128	147	157
3	142	185	183	200	137	134	150	145
6	130	177	188	173	127	143	145	145
12	147	173	177	155	132	137	145	134

\* Grown in pots containing 30 pounds of soil.

† In milligrams per 100 gm. fresh tissue.

In factorial pot experiments using tomatoes, spinach, and oats with four nitrogen, four manganese, and two potassium levels, it was evident that the influence of increasing amounts of one element on the formation of vitamin C is dependent on the level of other nutrients. As shown in table 6, under the conditions of this experiment, the vitamin C content of young oats was reduced when potassium was added to a soil deficient in potash. On the low-potash soil, also low or excessively high in manganese, increasing amounts of nitrogen reduced the vitamin C content. Where nitrogen was deficient, adding manganese greatly increased vitamin C, although the increase was greater on soil deficient in potash

than on soil amply supplied with potassium. The ascorbic acid was lowest where manganese was deficient or in excess and the soils received moderate applications of nitrogen. Results of Whitwer *et al.* (24) show that at high nitrogen levels, increasing the calcium supply reduced ascorbic acid, whereas at lower nitrogen levels the response to calcium was erratic. The manganese content of the plants is in an inverse proportion to the calcium applied, indicating that calcium affects availability of other elements. It would appear that, under optimum conditions, moderate amounts of lime or fertilizers will have little effect on the ascorbic acid content of the plant. When, however, some nutrient is deficient or is present in excess, the addition of other elements may cause a significant increase or decrease in vitamin content.

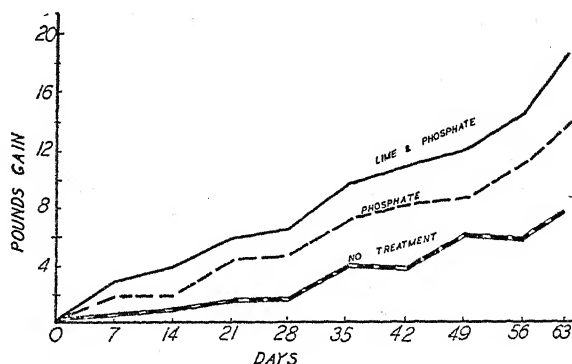


FIG. 1. RATE OF GAIN OF LAMBS FED CONSTANT AMOUNTS OF SOYBEAN AND LESPEDEZA HAY PRODUCED ON SOILS RECEIVING DIFFERENT SOIL TREATMENTS

#### ANIMAL ASSAYS OF LIMING

Animal feeding trials with forages and grains produced on untreated, fertilized, and limed and fertilized soils have shown consistent differences in animal response that cannot be accounted for by routine mineral analyses (5, 14, 20).

Limed and unlimed lespedeza hay grown three consecutive years and fed to sheep and rabbits have given animal responses much greater than the mineral and protein analyses of the forages would indicate (fig. 1). Liming had little effect on the calcium or phosphorus content of the forages. The protein was higher, however, and lignin and silica were lower where lime was applied. There is evidence<sup>1</sup> that a slight increase in lignin or silica (6) in a forage increases the quantity of feces voided by an animal and reduces the assimilation of minerals.

In addition to the difference in gain, the animal metabolism was altered. The wool from sheep receiving lespedeza hay from limed soil had a higher yolk content and was more shaggy and dirty. Analyses of the wools showed a higher fat content for the animals fed hay grown on limed soils. When the wools were scoured with a 1 per cent solution of alkali, that from animals receiving the hay

<sup>1</sup> Unpublished data of the senior author.



grown on unlimed soils was attacked and lost 34 per cent of its weight, whereas that from sheep receiving hay grown on limed soil lost only 24 per cent and remained soft and fluffy. Figures 2 and 3 show the appearance of these wools. Regardless of the chemical differences in these wools, it is significant that addition



FIG. 2. DIFFERENCES IN WOOL FROM SHEEP FED LESPEDEZA HAYS FROM UNLIMED AND LIMED SOIL

Left, hay from low-lime soil receiving only phosphate. Right, hay from limed soil receiving phosphate.

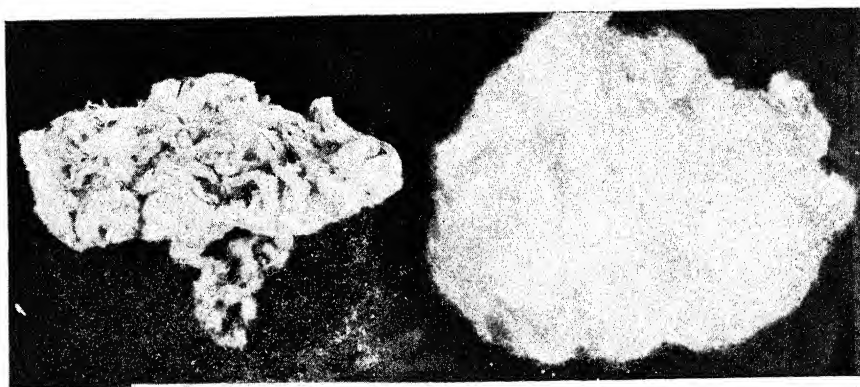


FIG. 3. SCOURED WOOLS FROM SHEEP FED LESPEDEZA HAYS FROM LIMED AND UNLIMED SOILS

Left, hay from soil receiving phosphate only. Right, hay from soil receiving lime and phosphate. After being scoured in 1 per cent potassium hydroxide, this wool could not be carded.

of lime to the soil brought about changes in plant composition not detected by laboratory analysis but reflected in rate of gain and in sufficient alteration in animal physiology to affect appearance and quality of wool.

Other investigations (14), in which forages grown on soils limed and unlimed

were fed to rabbits, showed a difference in animal growth and in bone size and density (figs. 4 and 5). Since there was also a difference in digestibility and utilization of minerals, these results are in agreement with other feeding trials (4) in which it was found that soil treatments influenced the quality of protein and that a slight increase in lignin content greatly reduced nutritive value. It appears that where forage growth is stunted by a deficiency of some plant nu-

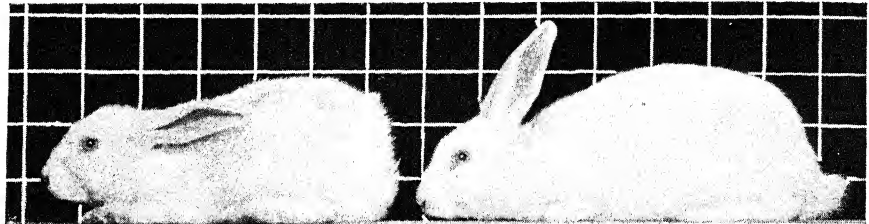


FIG. 4. ANIMAL RESPONSE TO FEED GROWN UNDER DIFFERENT SOIL TREATMENTS

Left, rabbit fed lespedeza from untreated soil. Right, rabbit fed lespedeza from soil treated with lime and phosphate.



FIG. 5. FEMURS FROM RABBITS FED LESPEDEZA HAY GROWN ON ELDON SILT LOAM UNDER DIFFERENT TREATMENTS

Left, no soil treatment. Right, soil treated with lime and fertilizer

trient, the biological values of the proteins are altered or the minerals and proteins are less efficiently assimilated.

#### INFLUENCE OF CALCIUM ON THE ENDOCRINE SYSTEM

That the calcium content of a feed can influence the endocrine system of animals has been shown by Campbell and Turner (3). They found that parathyroid glands of rabbits fed on bluegrass hay of low calcium content were nearly three times as large as those of rabbits fed legume hay as the principal consti-

tuent of the diet. This indicates that calcium applications to the soil that influence the calcium content of the feed would affect the parathyroid activity of animals consuming this feed. The possibility is suggested that other changes in a plant's physiology due to soil treatments might also exert different effects on the endocrine systems of consuming animals.

Calcium applied to the soil has influenced plant composition sufficiently to be manifest in the reproductive capacity of animals. Rabbits fed legume hay grown on a soil low in calcium became impotent. When hay from limed and fertilized soil was substituted, their potency was restored. As these forages differed but little in calcium content, it is possible that the potency change was due to the secondary effect of calcium on the absorption of other elements.

TABLE 7  
*Calcium content of milk received at a North Carolina army camp*

DAIRY	CALCIUM PER POUND OF MILK					Relation of average to NRC* value
	Sampled* Oct. 24	Sampled Oct. 30	Sampled Nov. 6	Sampled Nov. 12	Average	
	<i>mgm.</i>	<i>mgm.</i>	<i>mgm.</i>	<i>mgm.</i>	<i>mgm.</i>	<i>per cent</i>
A	492.0	492.3	482.9	489.2	489.1	91.4
B	520.9	541.9	476.6	476.6	504.5	94.2
C	445.3	453.7	498.3	470.1	466.8	87.2
D	516.9	480.2	530.0	470.1	499.2	93.3
E	578.9	483.8	552.3	480.2	523.8	97.9
Condensed Milk	....	....	....	....	1,078.1	99.5

\* Average composition as listed by the Food and Nutrition Board of the National Research Council = 535 mgm. per pound.

#### INFLUENCE OF SOIL TREATMENTS ON COMPOSITION OF ANIMAL PRODUCTS

Animal nutritionists are skeptical of assertions that the ration exerts a significant effect on the composition of meat or milk products. However, evidence exists that the capacity of a soil to supply nutrients is reflected through plants and affects the composition of animal products.

The calcium content of milk supplied by five dairies to a large army post in North Carolina was determined by the senior author (table 7). The milk was gathered from over a wide area, but most of it was produced in the Coastal Plain or Piedmont sections. Of the samples analyzed, 85 per cent showed a calcium content below the average listed by the Committee of Food Composition of the National Research Council. Two of the above-average samples were from one dairy. The lowest calcium content found was 17 per cent below the accepted average analyses. Samples of milk delivered to an army camp in Tennessee<sup>2</sup> were even lower in calcium, containing less than 350 mgm. per pound

<sup>2</sup> Personal communication from R. W. Simmons.

of milk. The values obtained by chemical analyses are considered accurate, as the same analytical procedure showed that the calcium content of condensed milk from high-calcium soil locations averaged 99.5 per cent of the National Research Council listing.

It was possible to obtain accurate information regarding the ration fed to animals at dairy C. These cows were fed grain from the Midwest and lespedeza hay and corn silage produced on unlimed Norfolk sandy loam. The lespedeza hay had a calcium content of 1.21 per cent and a phosphorus analysis of 0.11 per cent. The corn silage analyzed 0.19 per cent calcium and 0.04 per cent phosphorus. These values are below the average (17) for these crops, and it is significant that it was a regular practice, before the animals calved, for the veterinarian to give prophylactic injections of calcium-magnesium-boron glutonate to prevent milk fever.

It has been reported from Kansas (8) that beef produced on soils low in phosphorus had poorer keeping qualities and different chemical properties from those of beef produced on soils supplying an adequate amount of this element. Since the supply of calcium in a soil exerts much influence on availability of phosphorus, it is possible that the soil content of calcium is the primary factor influencing composition, with the availability of phosphorus, secondary.

#### SOIL CALCIUM AND HUMAN HEALTH

Information regarding the effect of food composition as influenced by soils is less positive for humans than for animals. The entire ration for animals may be grown on a single soil type, whereas modern transportation systems provide a wider variety of foods for human consumption and less chance of soil-influenced deficiencies. Although many of the currently publicized degenerative diseases are largely due to faulty selection of diet or loss of minerals and vitamins in food preparation, studies of Price (18) forcefully show that human health and soil regions are closely correlated. Reports of percentage rejection for armed service duty and reason for disqualification can be correlated with certain soil properties.

Although many factors influence human make-up and well-being, the nutrient-supplying capacity of the soils producing food determine the type of agriculture that can be supported and, to a large degree, the components of the diet. Calcium influences soil development, type of plants grown, and amount of protein and minerals that can be furnished for human diet, perhaps more than any other single nutritive element. Good health and progressive development of people are impaired when food must be obtained from soils low in this element.

#### DISCUSSION

The variable information obtained by different investigators of the effect of applied calcium on the composition of plants is due, among other factors, to failure of many investigators to consider the initial capacity of soil to supply plant nutrients. In most instances the effect of added calcium on the avail-

ability and absorption of nitrogen and minerals by plants completely overshadows changes that may result in the calcium absorbed.

If calcium is not a limiting element for the particular crop being grown, the amount added in lime or fertilizers may be such a small part of the total available as to have an insignificant effect on the composition of the plant. Where calcium is the only limiting element for plant growth, additions to the soil may fail to increase the percentage in the plant if increased growth is closely related to rate of absorption. Where growth is limited by a deficiency of some other element, additions of lime may increase the calcium content. When these variations are combined with differences due to balance of nutrients in soils, differences in plant species, in maturity, in methods of analyses, and other factors, it is apparent why one investigator obtains positive results and another negative.

It is accepted by both agronomists and animal nutritionists that in some soil areas crops may be so low in calcium as to produce deficiencies in animals consuming the feed. These deficiencies, however, have created only mild interest, since the mineral content of the ration may be cheaply increased by the addition of inorganic salts to the feed. Comparatively few investigators have considered that lime additions to a soil influence plants other than altering calcium content. It is accepted that the percentage saturation of the soil complex with calcium has a pronounced effect on availability of other soil minerals and biologic processes in the soil. This is confirmed by the influence of liming on the nitrogen content of plants and the quantity of other minerals absorbed. It has further been shown that soil treatments will alter the biologic value of proteins, or at least their efficiency of absorption by animals. With this variation in protein content, and the effect of calcium on the absorption of other elements, it is reasonable to assume that calcium added to the soil may directly or indirectly influence the formation of organic compounds within a plant and that these, in turn, will affect animal metabolism. Some investigators have obtained consistent differences in nutritive value of feeds due to soil treatments when measured by animal bioassays. Reports of animal preference for feeds grown under specific soil treatments are becoming numerous. Chemical differences in such feeds are frequently so small as to appear insignificant by routine analyses.

There is too much positive evidence on the influence of liming on the nutritive values of feeds to warrant considering all positive effects within the realm of experimental error. Differences may not necessarily be explained on differences in calcium content. It appears that one major influence of liming on plant composition is in altering the quantities of other nutrients absorbed from the soil and their effects on the plant, rather than in directly altering the calcium content. There is need of fundamental studies that consider soil properties and the level of nutrients within the soil, where crops grown are fed to animals and studies made of animal growth, reproduction, and composition. Until such information has been obtained under a variety of field conditions, the effect of calcium and other minerals on the nutritive value of plants will remain a controversial issue.



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# THE UPTAKE BY PLANTS OF PLUTONIUM AND SOME PRODUCTS OF NUCLEAR FISSION ADSORBED ON SOIL COLLOIDS<sup>1</sup>

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Very little is known about the fixation of plutonium and the products of nuclear fission by soils and about their absorption by plants. For obvious reasons no studies have ever been made with plutonium (Pu). The principal long-lived products of fission (Sr, Y, Zr, Cb, Ru, Te, Cs, Ba, La, and Ce) have not been proved essential to plant life, and for this reason they have been studied but little.<sup>3</sup>

Since the radioactive isotopes of these little-investigated elements are now available, their study has been greatly facilitated. In the present work, Pu and the fission products, Sr, Y, Zr, Cb, and Ce, have been adsorbed on a bentonitic clay and a sandy soil, and their absorption rates by selected test plants have been determined. The studies were divided into short-term and long-term experiments. For the short-term experiments, the activity was adsorbed on a suspended calcium bentonite clay. The test plant used in these experiments was barley. For the long-term experiments, the activity was adsorbed on a sandy soil, in which dwarf pea plants were grown. The sandy soil used was of the montmorillonitic type (base-exchange capacity = 5 m.e./100 gm.). In these studies the radio-elements were used without the addition of the inactive isotopes, i.e., the amount of the element involved was of the order of  $10^{-10}$  mols.

## EXPERIMENTAL

Calcium bentonite suspensions were prepared as follows: a 2.0 per cent suspension of electrodialyzed Wyoming bentonite was adjusted to pH 5.5 with saturated  $\text{Ca}(\text{OH})_2$  solution. Aliquots of the resulting Ca-bentonite suspension were diluted with distilled water to a concentration of 100 mgm. per liter. Following this, the radio-element was added in an amount corresponding to 10 microcuries per liter.

In each case, six 3-week-old barley plants, grown by the method of Hoagland and Broyer<sup>4</sup>, were placed in a quart jar containing 850 ml. of the suspension. The suspension was continuously aerated by means of compressed air. Three

<sup>1</sup> This document is based on work performed under Contract No. W-7405-eng-48 for the Manhattan Project and the information covered therein will appear in Division IV of the MPTS as part of the contribution of the Radiation Laboratory, University of California.

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<sup>3</sup> Robinson, W. O. Occurrence of rare earths in plants and soils. *Soil Sci.* 56: 1-6. 1943.

<sup>4</sup> Hoagland, D. R., and Broyer, T. C. General nature of the process of salt accumulation by roots with description of experimental methods. *Plant Physiol.* 11: 471-507. 1936.

jars of plants were set up for each element. The radio-elements used were Y, Ce, Zr + Cb, Te, and the three oxidation states of plutonium— $\text{PuO}_2^{++}$ ,  $\text{Pu}^{++++}$ ,  $\text{Pu}^{+++}$ . The Zr + Cb sample consisted of  $\text{Zr}^{95}$  in equilibrium with its Cb daughter.

Following a 24-hour absorption period, the tops were removed from the plants, and the roots were washed in running distilled water. The shoots and roots were dried at  $100^\circ\text{C}$ . and ground. The  $\beta$  and  $\gamma$  activities of the fission products were determined on suitable aliquots of the ground material. The samples were

TABLE 1  
*Absorption by barley plants\* of fission products and plutonium from clay suspensions*

ELEMENT	HALF-LIFE	RADIATION†	PERCENTAGE OF DOSE INITIALLY FIXED ON CLAY	ACTIVITY TAKEN UP BY ROOTS, PERCENTAGE OF DOSE	ACTIVITY TRANSLOCATED‡ TO LEAVES, PERCENTAGE OF DOSE
$\text{Y}^{91}$ .....	57 days	$\beta^-$ , no $\gamma$	98.8	27.7	0.104
$\text{Ce}^{141}$ .....	28 days	$\beta^-$ , $\gamma$	94.3	27.1	0.0303
$\text{Ce}^{144}$ .....	275 days	$\beta^-$ , $e^-$ , $\gamma$			
$\text{Zr}^{95} + \text{Cb}^{95}\S$ ..	Zr: 65 days Cb: 35 days	$\beta^-$ , $\gamma$ $\beta^-$ , $\gamma$	98.5	33.5	0.00310
$\text{Sr}^{90}$ .....	53 days	$\beta^-$ , no $\gamma$	60.4	10.7	1.60
$\text{Te}^{127}$ .....	90 days	$\beta^-$ , $e^-$ , x-ray	30.2	37.2	0.0415
$\text{Te}^{129}$ .....	32 days	$\beta^-$ , $e^-$ , $\gamma$ , x-ray			
$\text{PuO}_2^{++}$ .....	24,000 years	$\alpha$	18.6	37.8	0.010
$\text{Pu}^{++++}$ .....	24,000 years	$\alpha$	66.0	24.6	0.0024
$\text{Pu}^{+++}$ .....	24,000 years	$\alpha$	94.2	20.3	0.00045

\* Average fresh weight of leaves from six plants equals 1.75 gm.; dry weight equals 0.370 gm.

† The type of radiation tabulated includes short-lived daughters in equilibrium with parents.

‡ An assay of activity in the leaves showed the absence of radioactive impurities.

§ The Zr + Cb sample was an equilibrium mixture of the elements which had been isolated from a sample of fission products.

spread as uniformly as possible in milk-ashing capsules and counted with a mica window bell type counter tube. Appropriate corrections were made for the absorption within the sample. The  $\alpha$  activity of Pu was determined on the ash of the dried and ground material. The ash was spread in a very thin film, and the activity measured with a linear amplifier. The values for the uptake of activity are given in table 1. Portions of the initial suspensions were centrifuged in a McBain type spinning top centrifuge. The activity of the supernatant liquid was determined, and from this the amount of the radio-element fixed initially on the clay was calculated. These values are also given in table 1.

In the foregoing experiment the clay concentration was 100 mgm. per liter. In order to determine the effect of varying clay concentrations on the fixation of activity by roots, the following experiment was performed. The roots of barley plants, 2 weeks old, were immersed for 24 hours in a series of clay suspensions. Each suspension contained 10 microcuries of radio-Y. The clay concentration of the suspensions varied from 28.7 to 575 mgm. per liter. In each case six plants were used for 850 ml. of suspension and each concentration was tested in triplicate. Following the immersion period, the roots were separated from the tops, washed in running distilled water, dried, and counted. The results are presented graphically in figure 1.

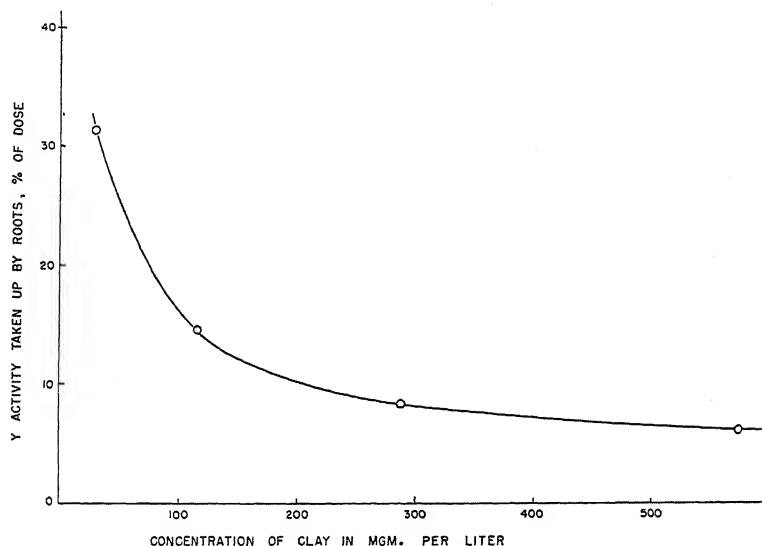


FIG. 1. EFFECT OF INCREASING Ca-BENTONITE CONCENTRATION ON ABSORPTION OF TRACE AMOUNTS OF Y BY BARLEY PLANTS

The soil experiments were performed in the following manner. Dwarf pea plants were grown for 3 months in the activated sandy soil in a greenhouse. The radio-elements used were Y, Ce, Zr + Cb, and Sr. Each treatment consisted of a pot containing one plant in 2,500 gm. of soil in which the radio-elements had been uniformly mixed. The treatments were run in duplicate. The initial activities of the various treatments were as follows:

Y-soil = 0.216  $\mu\text{c/gm.}$   
Ce-soil = 0.233  $\mu\text{c/gm.}$   
(Zr + Cb)-soil = 0.180  $\mu\text{c/gm.}$   
Sr-soil = 0.244  $\mu\text{c/gm.}$

At the conclusion of the experiment, the plants were separated into leaves, stems, pods, and roots, and quantitative determinations of activity made. A radioautograph was made of a leaf from one of the plants growing in the Sr soil (fig. 2). The activity of the various soils was also determined. The results, expressed in counts per second per gram, are given in table 2.

## DISCUSSION

With the test plants selected (barley) and under the conditions of the experiments, large fractions of the initial doses of Y, Ce, Zr + Cb, Sr, Te,  $\text{PuO}^{++}$ ,

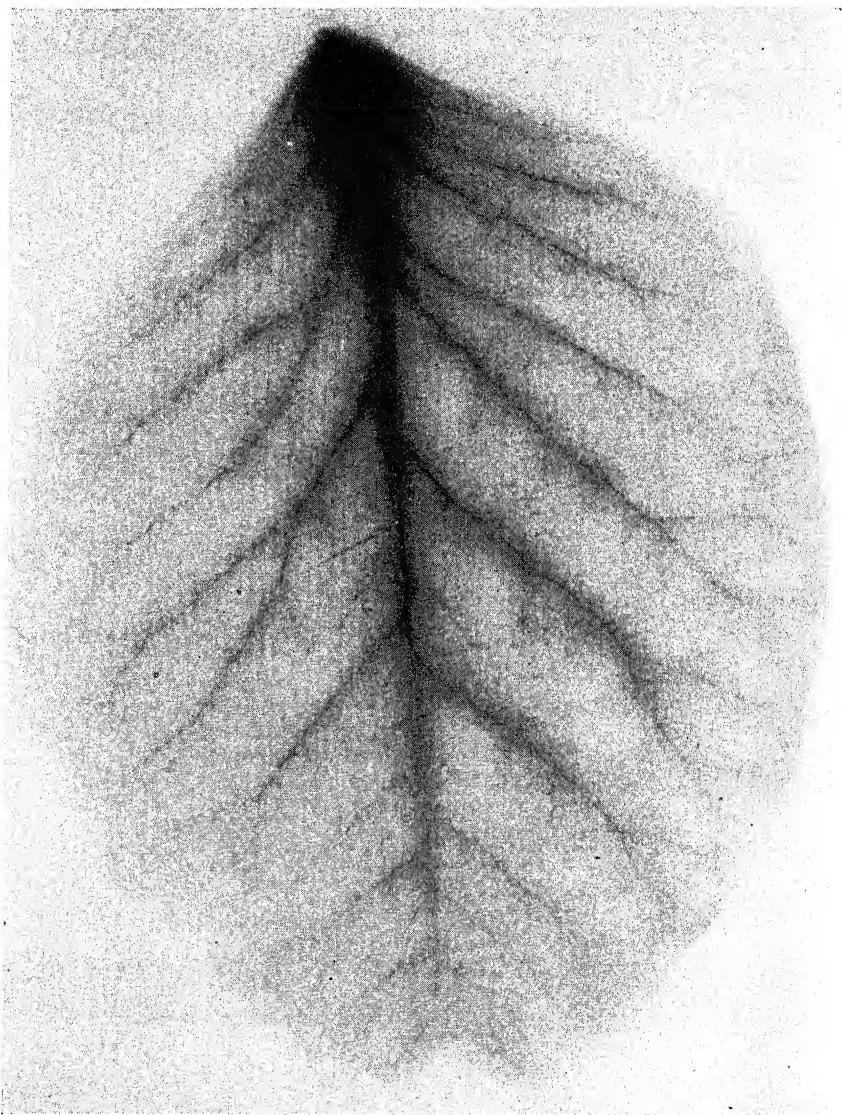


FIG. 2. RADIOAUTOGRAPH OF LEAF FROM DWARF PEA PLANT GROWING IN SOIL CONTAINING RADIOACTIVE Sr

$\text{Pu}^{++++}$ , and  $\text{Pu}^{+++}$  are either fixed or absorbed by the plants from clay suspensions. This fixation occurs primarily in or on the surface of the roots. For each element, some activity had been translocated to the shoots. This varied from 1.60 per cent of the initial dose for Sr to 0.00045 per cent for  $\text{Pu}^{+++}$ .



The nature of the fixation of activity by the roots in the short-term experiments is as yet unelucidated. This fixation cannot be accounted for by the adherence of clay particles to the roots, since essentially all of the added clay was recovered by washing the roots even when as much as 35 per cent of the dose was fixed. Since the amounts of Y, Ce, Zr + Cb, and Pu<sup>+++</sup> in true solution were small com-

TABLE 2  
*Absorption by dwarf pea plants of fission products from soil*

ELEMENT	SAMPLE	TOTAL DRY WEIGHT	ACTIVITY	REMARKS
		gm.	counts/sec./gm.	
Y	Soil	2500	290	Marked signs of injury in roots and tops
	Leaves	2.74	10.0	
	Stems	1.88	1.55	
	Seeds	1.90	0.02	
	Pods	1.93	0.80	
	Roots	5.0*	385	
Ce	Soil	2500	765	Marked signs of injury in roots and tops, particularly in roots
	Leaves	1.80	17.0	
	Stems	1.71	3.68	
	Seeds	1.68	0.13	
	Pods	1.90	1.98	
	Roots	5.0	662	
Zr + Cb	Soil	2500	277	Roots severely injured, tops noticeably injured
	Leaves	3.01	7.09	
	Stems	2.67	2.30	
	Seeds	1.54	0.30	
	Pods	2.22	2.28	
	Roots	5.0	418	
Sr	Soil	2500	346	Roots and tops in extremely poor condition
	Leaves	1.53	2605	
	Stems	1.88	1905	
	Seeds	1.61	72.5	
	Pods	2.28	1115	
	Roots	5.0	3530	

\* As it was not feasible quantitatively to separate the roots from the soil, the weights of the roots was estimated. It should, however, be pointed out that the counts/sec./gm. values for the roots were accurately determined.

pared to the amounts fixed by the roots, there must necessarily have been a release of the elements from the clay particles to the roots. That is, for these elements roots can compete successfully with clay particles. Presumably this transference from the clay particles to the roots could occur by contact exchange<sup>5</sup> or by hydrolysis of the adsorbed element and subsequent uptake from the solution.

<sup>5</sup> Jenny, H., and Overstreet, R. Surface migration of ions and contact exchange. *Jour. Phys. Chem.* 43: 1185-1196. 1939.

Figure 1 shows that with increasing clay concentration the competition for the radioelement (Y) becomes less favorable for the roots. The graph shows further that even with extremely minute quantities of the element, the clay content can be increased considerably without rendering the element unavailable. According to figure 1, a point is reached beyond which further increases in clay content have little effect upon the uptake.

The soil experiments were in close agreement with the short-term tests. For all treatments the highest concentration of activity was found in the roots. In common with the short-term tests, some activity was found in the tops for all elements tested. Here again, translocation to the top was especially pronounced for Sr. For all elements tested the activity in the tops was localized primarily in the leaves and to a lesser degree in the stems. The seeds were relatively inactive. The ratioautograph of a leaf from a Sr test plant (fig. 2) shows that at least with trace amounts the activity is largely localized in the veins.

In every case the soil contained sufficient activity to cause marked injury to the plants. For Y, Ce, and Zr + Cb this direct injury was confined to the roots. For Sr, which was readily translocated, the tops were also suffering from radiation injury. For those elements which injured only the roots, there were indications that the water and nutrient uptake were seriously curtailed. From these experiments it appears that a mean activity of approximately 0.1 microcurie per gram soil at the region of contact with the roots acting over a period of 3 months results in marked injury to the plants.

#### SUMMARY

Barley and pea plants have been found to take up the fission elements Y, Ce, Zr + Cb, Te, Sr, and the three valence states of Pu, even when these elements are present in trace amounts on the surfaces of clay or soil particles.

For all the elements tested, the greatest fixation is in or on the roots. With the exception of Sr, translocation occurs only to a limited extent. The translocation of Sr is relatively large.

Activity levels of 0.1 microcurie per gram soil are sufficient to cause very pronounced injury over a 3-month period.

## THE HARDPAN IN CERTAIN SOILS OF THE COASTAL PLAIN

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It is generally assumed that hardpans in soil profiles are genetic horizons irreversibly cemented by some binding material such as free silica or iron oxides. In some soils, however, the hardpan is not a pedogenic horizon but may represent a condition inherited from a former land surface which escaped obliteration by contemporary soil-forming process. In many cases, moreover, the hardpans, whether pedogenic or relic, are uncemented by any binding material other than clay and are hard simply because of physical compaction. These pans may become very hard when dry and soften somewhat when moist.

The compacted and apparently uncemented hardpans are common in some soils of the Coastal Plain, such as those of the Leonardtown series. The Leonardtown series formerly included soils developed under rather wide range of drainage. Recently these soils were reclassified, and the Beltsville series was established to include the soils of better drained areas, whereas the Leonardtown series was limited to the soils of inadequate drainage. Since these changes have not been published yet, the name *Leonardtown soils* throughout this paper refers to the soils as described by Marbut in *Soils of the United States* (see footnote 5).

The Leonardtown soils are developed from stratified parent material. In such soils it is difficult to separate profile characteristics which are due to soil formation from those inherited from the parent material; in fact, such soils may have hardpans partly related to stratification and partly to soil-forming processes. Obviously, these soils are not ideal for the study of the genesis of hardpan. Nevertheless, the pans of these soils represent a peculiar type of formation fundamentally different from the development of the chemically cemented hardpans.

Seven profiles of Leonardtown silt loam in Prince Georges and Montgomery Counties, Maryland, were examined, and samples were collected for laboratory investigations. Some profiles were examined at different seasons, and one pit was kept open for a year to observe changes in the pan under different moisture conditions. Laboratory investigations included mechanical analysis, differential thermal analysis of the clay, mineralogical analysis of the very fine sand and coarse silt fractions, studies of thin sections of all horizons supplemented by the electron microscope examination, and various other experiments and measurements. Moisture samples were taken at each pit. Continuous records of soil moisture and temperature changes in different horizons during several months were obtained in one pit by the thermal conductivity method of Shaw and

<sup>1</sup> Soil scientist, soil scientist, and associate soil scientist, respectively, Bureau of Plant Industry, Soils, and Agricultural Engineering. The authors are indebted to S. B. Hendricks for helpful suggestions and criticism.

Baver<sup>2</sup>. Special emphasis in all these studies was placed on attempts to determine the character of the hardpan and the causes of its hardness.

#### LEONARDTOWN SILT LOAM

##### *Parent material*

The Coastal Plain is built of stratified, commonly unconsolidated but locally cemented, gravelly sediments ranging in age from Lower Cretaceous to Pleistocene. The sediments of Miocene age and older are truncated by a series of terraces which slope gently seaward. The gravelly sediments of the higher and older terraces in Maryland are covered in places by a layer of gravel-free material ranging in thickness from a few inches to more than 10 feet. The thickness and general character of such a covering are more or less uniform on the relatively level and undissected remnants of the old terraces, whereas in the eroded sloping areas it might be absent entirely.

Material of the uppermost part of the mantle in many places consists predominantly of silt and is said to resemble loess both in texture and color. The silty layer averages about 2 feet in thickness, commonly ends rather abruptly, and is underlain by a decidedly coarser and less assorted material which may include occasional pieces of gravel. The second layer grades into the underlying stratified material without a sharp line of demarcation<sup>3</sup>.

The Leonardtown soils are developed from these gravel-free sediments under mixed pine-and-oak forest on relatively level, undissected parts of the older terraces with a rather impeded drainage (figs. 1 and 2).

##### *Profile*

Leonardtown silt loam, the most common type of the series, is characterized by the following profile (fig. 3)

- A<sub>0</sub>—about 2 inches thick, dark gray to black, consists of well-decomposed soft leafmold with admixture of gray fine sand; thoroughly interwoven by roots; pH 4.
- A<sub>1</sub>—usually absent; when present is less than 2 inches thick, dark gray or brownish gray fine sandy loam.
- A<sub>2</sub>—10 inches thick, ranging from 6 inches to about 1 foot, very light brownish or yellowish gray silt loam; mellow when moist, slightly plastic when wet and crumbly when dry. Near the surface, it has a moderately developed fine platy structure, which fades with depth. Lower boundary is fairly distinct and smooth.
- B—8 inches thick, ranging from 6 to 10 inches, light brown silty clay loam or clay loam, in some places with pronounced yellowish tint; rather compact; sticky when wet. In dry condition it shows weakly developed medium to coarse blocky structure.

<sup>2</sup> Shaw, B. T., and Baver, L. D. 1939 An electrothermal method for following moisture changes of the soil in site. *Soil Sci. Soc. Amer. Proc.* 4: 78-83. These measurements were made by E. F. Miles in connection with his experiments on the perfection of this method.

<sup>3</sup> There is no general agreement about the origin of these sediments. Miller of the Maryland Geological Survey suggested that toward the end of accumulation of the Coastal Plain sediments the velocity of streams decreased so that gravel no longer could be carried by them and a sheet of finer material was spread over the older formations [Maryland Geological Survey, Prince Georges County].

H— (the hardpan) about 28 inches thick, ranging from about 2 feet to about  $2\frac{1}{2}$  feet. The upper boundary of the pan is rather sharp. It is commonly encountered at a depth of about 20 to 24 inches. At the top of the pan there is usually a layer 2 to 5 inches thick, conspicuous for its fairly well developed coarse platy structure, high content of



FIG. 1. NATIVE VEGETATION ON LEONARDTOWN SILT LOAM



FIG. 2. GENERAL VIEW OF THE BRANDYWINE TERRACE IN THE VICINITY OF BRANDYWINE, MARYLAND, A TYPE-LOCATION OF LEONARDTOWN SILT LOAM

silt, and horizontally banded light gray and brown color. This layer belongs neither to the pan, from which it differs in consistency, nor to the B horizon, from which it differs in structure and color. According to its mechanical composition it is a part of the silty upper part of the mantle, from which the A and B horizons are developed, rather than of the pan material.



The hardpan consists of slightly mottled very light gray silt loam usually with pronounced brownish tint. Its texture, however, varies from place to place from coarse sandy loam to clay loam and generally is somewhat coarser and more heterogeneous than the texture of the upper horizons; commonly it becomes coarser toward the base of the pan. Scattered pieces of gravel and occasional small pockets of fine gravel are not uncommon in the lower part of the pan.

The pan is most strongly indurated at the top beneath the platy layer. Its hardness gradually diminishes with depth. The color of the lower half of the pan becomes somewhat darker and more variegated with rather bright rusty mottlings, which also increase with depth.

A conspicuous characteristic of the pan is the presence of roughly vertical, irregular light-colored streaks which begin below the laminated layer at the top and extend to







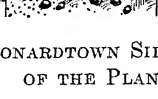
	INCHES		SAND	SILT	CLAY	GRAVEL	VOLUME WEIGHT
A <sub>2</sub>	10		15.5	69.5	15.0	0	1.47
B	20		13.1	61.6	25.3	0	1.53
			17.9	56.1	26.0	0	1.52
H	30		40.0	39.6	20.4	0	1.80
			59.8	28.7	11.5	2.0	1.87
C	60		57.9	18.7	23.4	5.0	1.76
			67.6	13.6	18.8	26.1	

FIG. 3. LEONARDTOWN SILT LOAM. PROFILE 6, SAMPLE TAKEN 4 MILES NORTHEAST OF THE PLANT INDUSTRY STATION, BELTSVILLE, MARYLAND

its base (fig. 3). At the top the streaks are up to 1 inch wide, their width gradually decreasing with depth to the vanishing point near the bottom of the pan. Some of them branch downward like roots. The core of the streaks is formed of a rather dark brown clay enclosed between the bleached walls, outside of which the hardpan material is colored rusty orange.

In a horizontal plane the streaks form an irregular polygonal pattern (fig. 4) with polygons about 2 feet in diameter (fig. 5). This pattern is sharp and conspicuous at the top of the hardpan. With depth, the streaks become thinner, less distinct, and more irregular, so that about 18 inches below the pan surface the polygonal pattern virtually disappears, being replaced by irregular, disconnected, and indistinct veins and mottlings (fig. 4-D).

No open cracks in the hardpan were seen even in dry soil, but cleavages along the planes of the streaks were clearly demonstrated. Splitting of the hardpan along the cleavage shows a moist glistening surface heavily coated with dark gray clay over which are distributed imprints of living roots.

In general, roots, except for the finer ones common in the streaks to the very base of the pan, do not penetrate the hardpan. All the pits, however, were dug at a distance from large trees and stumps, and it is not known how roots are distributed under and in the immediate vicinity of the stumps.

- C—The material below the hardpan usually is much coarser in texture and more variegated in color than the overlying layers. The content of unsorted gravel increases rather sharply. The texture of the matrix ranges from coarse sand to clay. Usually it is a heterogeneous mixture of sand, silt, and clay. A bright red mottling, more pronounced

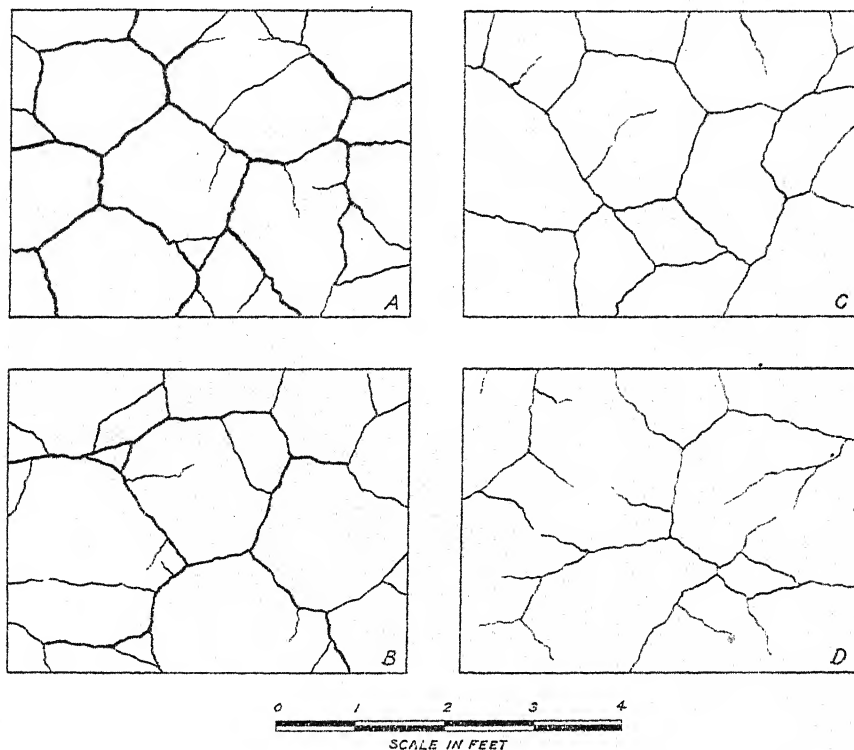


FIG. 4. POLYGONAL PATTERN OF STREAKS IN THE HARDPAN OF LEONARDTOWN SILT LOAM (PROFILE 7)

A—at the top of the pan; B, C, and D—the same pattern 6 inches, 12 inches, and 18 inches, respectively, below the pan surface. Drawn with the aid of Saltzman's vertical overhead reflecting projector from Kodachrome photographs.

in materials of fine texture than in sands, appears below the hardpan and increases in density and brightness with depth.

The material in this horizon obviously represents a different layer of the stratified sediments and does not represent the unmodified parent material of the Leonardtown soil.

#### *Mechanical composition*

The data in table 1 show several significant breaks in mechanical composition of this soil. A sharp change in content of gravel should be noted at a depth of 4 feet, which is the base of the hardpan (fig. 3). Above this level the material

is virtually free of coarse gravel ( $>2$  mm.) and contains little fine gravel (2–1 mm.). This is the boundary between the older stratified sediments and the more recently deposited material. A conspicuously high content of silt ranging from about 60 per cent to more than 70 per cent in the upper part of the soil overlying the hardpan decreases abruptly at a depth of about 2 feet. Starting from below the platy layer, the content of sand (1–0.05 mm.) increases with depth.



FIG. 5. DETAILS OF A SINGLE POLYGON AT THE SURFACE OF THE HARDPAN  
(LEFT CENTER IN FIGURE 4-A)

Drawn with the aid of Saltzman's vertical overhead reflecting projector from a Kodachrome photograph.

The clay content of the B horizon is significantly higher than that of any other layer of the profile. It is nearly double the content of the A horizon and considerably higher than in the hardpan. This increase in the B horizon may or may not be due to stratification of the original material. This horizon is underlain by the impervious hardpan and may represent the claypan. Its high content of clay might be due in part to eluviation but more specifically to the formation of clay in place by differential hydrolysis.

The relatively low clay content of the hardpan is particularly interesting because it eliminates clay as a dominant cementing agent. The mechanical composition of the material in the streaks which break the hardpan into polygonal

blocks is markedly different from that of the blocks. It was found that the clay content of the brown central cores of streaks averages about 60 per cent and in some instances approaches 100 per cent. The bleached walls of the brown cores contain about 33 per cent clay, whereas the hardpan near the bleached streaks contains, on the average, only 18 per cent clay.

Mechanical analysis of several other profiles, the results of which are not included in this paper, show essentially the same size distribution of particles. These data very strongly suggest that the gravel-free sediments from which the Leonardtown soils develop consist of two strata, the upper more or less loess-like and the lower more sandy with a rather heterogeneous mechanical composition.

TABLE 1  
*Mechanical composition of Leonardtown silt loam (profile 6)\**

DEPTH	pH	GRAVEL 2 MM.	COARSE SAND 2-0.5 MM.	MEDIUM AND FINE SAND 0.5-0.1 MM.	VERY FINE SAND 0.1-0.05 MM.	COARSE SILT 0.05-0.02 MM.	FINE SILT 0.02-0.002	CLAY 0.002 MM.
<i>inches</i>			<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
0-1	4.2	0.0	7.3	7.1	5.6	21.0	45.2	13.8
1-4	4.2	0.0	4.6	5.7	5.4	20.7	48.5	15.1
4-8	4.1	0.0	4.2	4.5	4.4	18.2	49.1	19.7
8-12	4.3	0.5	3.4	4.0	4.7	22.6	52.7	12.6
12-19	4.5	0.0	3.7	4.4	5.0	19.2	42.4	25.3
19-24	4.7	0.0	6.4	5.6	5.9	17.9	38.2	26.0
24-32	4.4	0.0	16.7	11.9	11.4	12.2	27.4	20.4
32-48	5.1	2.0	25.8	17.5	16.5	11.3	17.4	11.5
48-72	4.8	5.0	30.7	15.3	11.9	8.2	10.5	23.4
72-74	4.7	26.1	35.4	19.5	12.7	7.8	5.8	18.8

\* Sample taken 4 miles northeast of the Plant Industry Station, Beltsville, Md. Analysis by Elmer Simpson.

It is evident that the parent material of the Leonardtown hardpan differs in origin from that of the A and B horizons of this soil.

#### *Mineralogical composition*

The sand in Leonardtown silt loam is 97 to 99 per cent quartz and the non-quartz content of the coarse and fine silt is only slightly greater. Heavy liquid separations were made in acetylene tetrabromide at specific gravities 2.92 and 2.70 on the 0.1-0.05 mm. and 0.05-0.02 mm. fractions. Separates were mounted in balsam or piperine and percentage frequency of minerals was determined by counting a large number of fields.

The weight percentage of heavy minerals is very low, ranging from less than 0.5 per cent to slightly over 3 per cent in the very fine sand and from 2 to 5 per cent in the coarse silt. The content of heavy minerals increases in most cases with depth down to the top of the hardpan and decreases through the pan and below it. Significance of weight percentages of heavy minerals is obscured by the large amount of secondary iron minerals in the B horizon and the pan.

The light separates (table 2) are composed essentially of quartz. The feldspar consists largely of orthoclase with a little microcline and an occasional grain of plagioclase. Mica is chiefly muscovite with a small amount of weathered biotite<sup>4</sup>.

The distribution of feldspar and mica, especially a sharp decrease in content of these minerals below the surface of the hardpan, is further evidence that the material of the hardpan was not derived from the same source as that of the A and B horizons. It is conceivable that a high water table could have been responsible for removal of these minerals from the deeper horizons of the soil by solution, but if considered with the rest of the data, this seems to be the least likely explanation.

The relative proportion of the important minerals in the heavy mineral separate is given in table 3. Approximately half of the fraction consists of opaque, weathered, and secondary minerals which could not be identified. In the B

TABLE 2  
*Mineralogical composition (light minerals) of very fine sand and coarse silt in Leonardtown silt loam (profile 6)*

DEPTH	VERY FINE SAND (0.1-0.05 MM.)			COARSE SILT (0.05-0.02 MM.)		
	Quartz	Feldspar	Mica	Quartz	Feldspar	Mica
<i>inches</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
1-4	96.9	0.8	2.1	91.2	5.5	2.1
4-8	93.0	1.1	5.8	90.8	6.5	2.1
8-12	78.8	2.0	18.8	89.5	6.3	3.6
12-19	79.3	3.2	17.4	83.0	6.2	9.4
19-24	88.2	2.1	9.7	84.6	8.7	6.0
24-32	99.1	0.6	0.2	89.0	5.0	5.3
32-48	99.6	0.2	0.0	93.6	4.0	1.9
48-72	99.7	0.2	0.0	98.2	0.6	0.7

horizon and the hardpan, scaly reddish brown iron oxide minerals were prominent.

Of the identifiable heavy minerals, zircon, tourmaline, and epidote are the most important. There is no significant variation in the zircon-tourmaline ratio throughout the soil profile, though in the lower part of the hardpan and below the pan the zircon includes more fragments of broken large crystals rather than the small euhedra and the proportion of brown tourmaline increases relative to the blue-green variety.

The rutile group includes rutile, cassiterite brookite, and an occasional monazite. No significant variations in the proportion of any of these minerals in different soil horizons were noticed.

<sup>4</sup> The high content of mica in profile 6 may be accounted for by the location of the sampling area, which was only  $\frac{1}{4}$  of a mile from the edge of the Piedmont where the soils are micaceous and outcrops of micaceous schist are numerous. In the other profiles of Leonardtown silt loam the mica content was found to be considerably lower.



The amphibole-pyroxene group includes mainly actinolite and tremalite with some enstatite, and occasional diopside. In the miscellaneous group are silimanite, kyanite, topaz, andalusite, chlorite, and some biotite.

The distribution of epidote is roughly constant down to the top of the hardpan. Below this depth the epidote content drops to one third and finally to one seventh of that in the upper horizons developed from the silty material. It is hardly possible that such a sharp decrease in the epidote content below the surface of the hardpan was due to chemical weathering, because any process which could have removed so much epidote would have been severe enough to break down virtually all amphiboles and pyroxenes as well as kyanite and silimanite, which are present in small amounts in all horizons. Hence, the epidote distribution as well as distribution of feldspar and mica lends support to the assumption that the parent material of the Leonardtown hardpan has a different

TABLE 3

*Mineralogical composition (heavy minerals)\* of very fine sand in Leonardtown silt loam (profile 6)*

DEPTH	ZIRCON	TOURMALINE	RUTILE GROUP	EPIDOTE	STAUROLITE	AMPHIBOLES AND PYROXENES	MISCELLANEOUS, PARTLY MICA
<i>inches</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
1-4	16.4	18.3	9.6	22.2	7.5	12.5	8.6
4-8	24.2	20.7	15.0	16.7	4.5	5.0	10.0
8-12	22.7	22.2	17.4	12.8	5.5	2.6	17.5
12-19	17.7	17.7	21.3	15.5	5.3	6.2	16.6
19-24	28.8	13.0	14.1	13.4	4.0	5.8	12.0
24-32	37.4	21.1	17.0	3.5	7.5	1.5	13.1
32-48	29.5	32.5	14.2	2.3	9.7	1.1	10.6
48-72	36.0	27.9	16.6	2.0	5.6	1.6	10.2

\* Opaque, weathered, and secondary minerals are omitted.

source and probably was laid down at a different time and under different conditions from those of the parent material of the upper part of the profile.

The results of the thermal analyses of the clay  $< 2 \mu$  (fig. 6) show about 15 to 25 per cent of kaolinite in the clay of the upper horizons of the soil, increasing to about 40 per cent in the clay below the hardpan. There is no significant difference in the composition of the clay in the upper horizons and the hardpan. The clay below the pan, however, is different. Besides the relatively high kaolinite content, the thermal analysis shows a trace of gibbsite in this material. As pointed out in the description of the soil, a pronounced red mottling appears below the hardpan. Such a mottling and the presence of gibbsite suggest a possibility of a slight laterization of this material. In the places from which samples for this study were taken, the thickness of the gravel-free sediments is about equal to the combined thickness of the upper soil horizons and the hardpan. Thus, the traces of laterization appear in the material of the older formation

underlying the more recent gravel-free mantle. Leonardtown silt loam itself is a podzolic soil<sup>5</sup> and presumably not affected by laterization.

*Some physical characteristics of the hardpan*

Direct examination of hardpan in the field suggests that its hardness is not due to cementation. This was further demonstrated by several simple experiments.

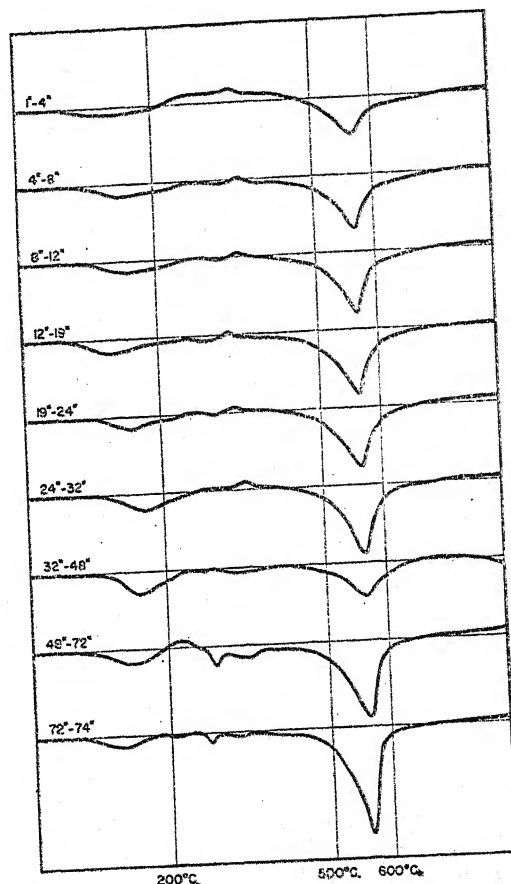


FIG. 6. DIFFERENTIAL THERMAL ANALYSIS OF THE CLAY  $< 2 \mu$  IN DIFFERENT HORIZONS OF LEONARDTOWN SILT LOAM

Lumps of pan submerged in water or in contact with water disintegrate completely and almost instantaneously (fig. 7). Such rapid slaking would not be expected if the pan were cemented. It was observed that the pan is virtually impervious to water, being only damp at times when the A<sub>2</sub> and B horizons were waterlogged. In such a condition the hardpan becomes somewhat softer than

<sup>5</sup> Marbut, C. F. 1936 Soils of the United States. Atlas of American Agriculture, Part III, p. 34. Washington, D. C.

during the dry periods in summer and fall. Whatever water penetrates the pan apparently moves through the cleavages, and its lateral movement is very slow<sup>6</sup>.

It was found that blocks of pan material kept under normal air conditions retain their original hardness and color for at least 14 months. Such blocks can be crushed only under very strong pressure. However, blocks kept for a few weeks in an atmosphere of 100 per cent humidity or moistened by capillarity and then dried, become friable and are easily crushed between the fingers. After one or more wettings and dryings, blocks become much more permeable to water. These experiments demonstrate the lack of cementation of the pan and lend support to the belief that its hardness largely depends upon a rather close packing of the primary particles and, perhaps, their interlocking orientation during deposition. Measurements of volume weight also support this assumption.

The volume weight of the oven-dry samples of the hardpan is significantly higher than that of the overlying material—1.87 as compared with 1.53 and 1.52

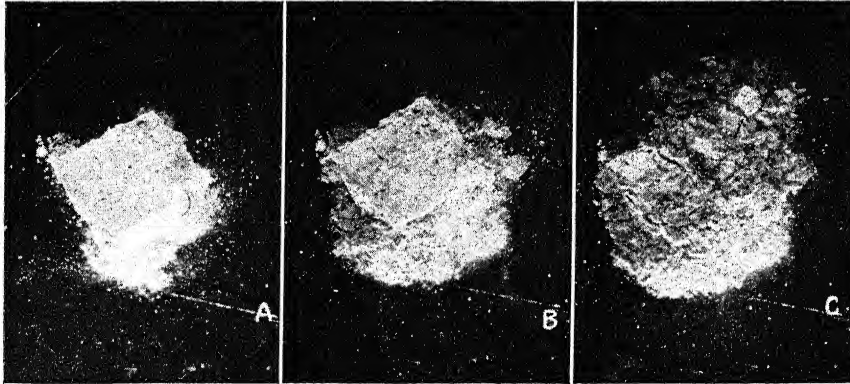


FIG. 7. DISINTEGRATION OF LUMP OF LEONARDTOWN HARDPAN IN WATER  
A—Immediately after submersion; B—30 seconds later; C—1 minute later.

for the A<sub>2</sub> and B horizons, respectively. The porosity of the hardpan is approximately 30 per cent and indicates an extremely close packing of the particles.

To investigate more closely the fabric of the hardpan in comparison with that of other horizons, thin sections of these materials were made<sup>7</sup> and were examined under low magnification.

<sup>6</sup> A pit was dug to a depth below the base of the pan in 1938 and refilled with crushed material after the soil profile had been described. Seven years later another pit was dug at the same spot across the former one in such a way that at both ends it exposed the vertical walls of the old pit. These walls had been in contact with the filling for 7 years, during which the hardpan cut by the former pit could have been affected by moisture circulating through the porous refill material. It was found that a lateral modification of the pan extended for only 2 inches back from the walls of the old pit.

<sup>7</sup> Thin sections were prepared according to the procedure of Ross [Ross, C. S. 1924 A method of preparing thin sections of friable rock. *Amer. Jour. Sci. (Ser. 5)* 7: 483-485], using Bakelite varnish as the impregnating substance. In the case of incoherent materials, such as soils, special precautions are needed for the preparation of a satisfactory thin sec-

Figure 8 (*A* and *B*) shows vertical sections of the hardpan from profiles 5 and 6, the latter having a much coarser texture than the former. The white spots are all quartz grains. Because of absence of prismatic or platy grains, there is no orientation or imbrication effect among the sand and silt grains. Segregation of coarse grains into a layer suggesting water-sorting of the material can be seen in *A*. Such effects were seen also in the coarse pan of profile 6, but in such broad bands that they could not be included in one microscope field. The particles are packed with no visible pore space. Successively smaller voids are filled with successively smaller particles.

The small amount of clay in the hardpan is segregated in small pockets and especially the cracks. Figure 8-*E* shows a clay-filled small vertical crack, and *F*, a thin section of the clay filling in one of the large cracks. Close examination with polarized light showed that the clay is commonly oriented in layers parallel to the walls of the cracks.

In contrast to the coarse texture and close packing of the hardpan, *C* and *D* (fig. 8) show the porous condition of the silty material in the platy layer above the pan and in the  $A_2$  horizon, respectively. The white horizontal streaks in the first picture and most of the smooth bordered white spots in the second are voids. Distribution of the voids in the  $A_2$  horizon suggests a horizontal arrangement, although the platy structure of this horizon is much less distinct than that of the layer above the pan.

#### *Moisture relationships*

The data already presented demonstrate that the hardness of the pan in the Leonardtown soil depends largely, if not entirely, upon the close packing of interlocking particles and is maintained in its natural condition mainly by the relative impermeability of the pan to water. Changes in consistency of the pan in the laboratory experiments apparently took place because the small lumps of pan material used were free to expand as a result of the pushing apart of the particles by soaking water. This cannot take place in the field. A lump of hardpan that was free to expand might absorb more water than an equal volume of the pan material in the undisturbed soil. Even thorough saturation of the undisturbed

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tion. Small blocks of undisturbed soil must be completely air-dry, preferably at less than 40 per cent humidity. The blocks of friable soil should be reinforced by painting with Bakelite varnish diluted with acetone to a watery consistency. After this the blocks should be allowed to dry and then baked at 100° C. for 4 to 8 hours. The blocks can then be trimmed with a fine hacksaw or carborundum saw to a suitable shape and size and thoroughly impregnated with a slightly thicker solution of Bakelite varnish by immersing the samples in varnish in small bottles and evacuating. Impregnated samples are dried in air until the solvent has evaporated, then baked in an oven at 100° C. for about 12 hours. Higher temperature or longer heating causes the varnish to darken to a deep brown.

Thin sections are ground according to the same procedure used in making thin sections of rocks. If the chip shows a tendency to loosen while being ground, additional coats of varnish may be applied to the surface as the section approaches completion. With friable soil material, especially if much clay is present, it may be difficult to obtain a thickness of less than 0.05 mm. as estimated from the interference color of the minerals.

hardpan allows only limited absorption of water without any disintegrating effect and only slight decrease of the original hardness.

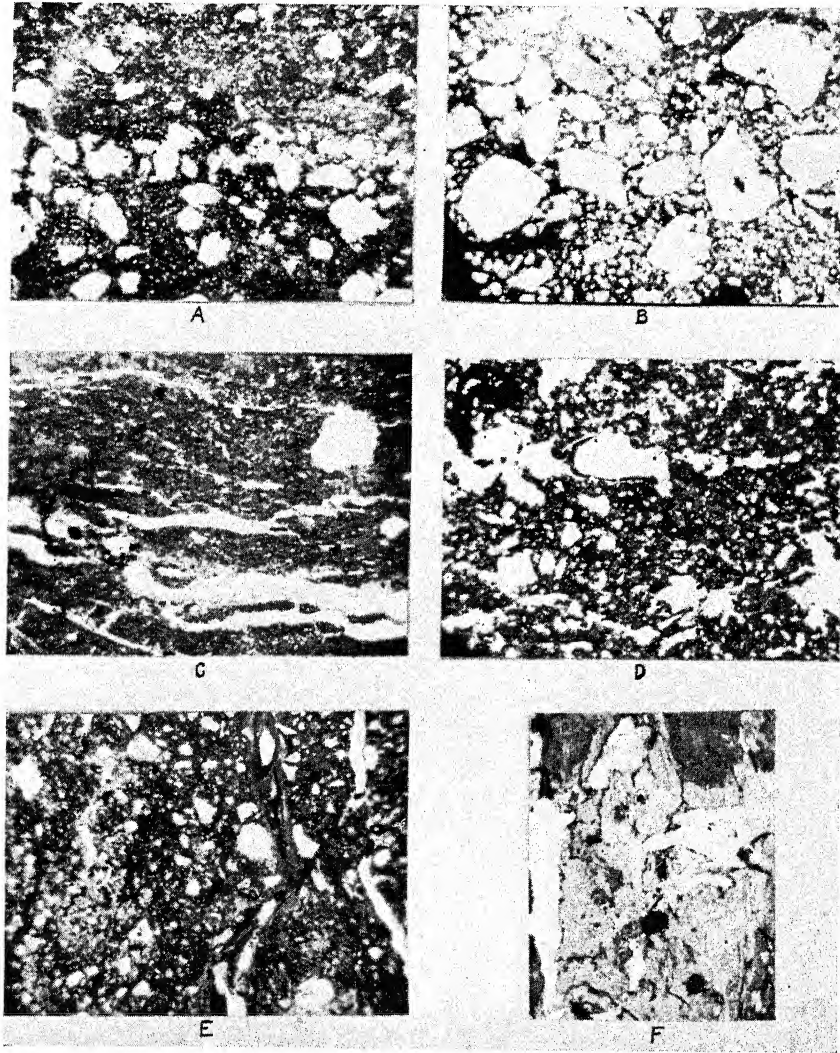


FIG. 8. VERTICAL CROSS SECTIONS OF MATERIALS FROM DIFFERENT HORIZONS OF LEONARDTOWN SILT LOAM

*A*—hardpan from profile 5; *B*—hardpan from profile 6; *C*—silty material in the platy layer above the hardpan from profile 6; *D*—silty material from the  $A_2$  horizon; *E*—clay-filled crack in the hardpan; *F*—clay filling in a large streak. Magnification about 15 times.

Moisture determination in samples taken from the fresh pits showed that the pan is usually drier than materials above and below it, with the probable exception of the *A* horizon during the dry summer months.

An effort was made to obtain continuous moisture measurements in the various



horizons of the Leonardtown soil (profile 6) by the thermal conductivity method (see footnote 2). The method and our technique of application are still open to criticism, but improvements in the elements and in their installation lead us to believe the results are valid though not precise. Elements were placed in seven horizons horizontally from the vertical wall of the pit at a distance of 3 feet from the wall. After installation, the wall was sealed by paraffine. For simplification, the results of only four measurements are presented in figure 9. These data convincingly show that the moisture content of the hardpan is the lowest

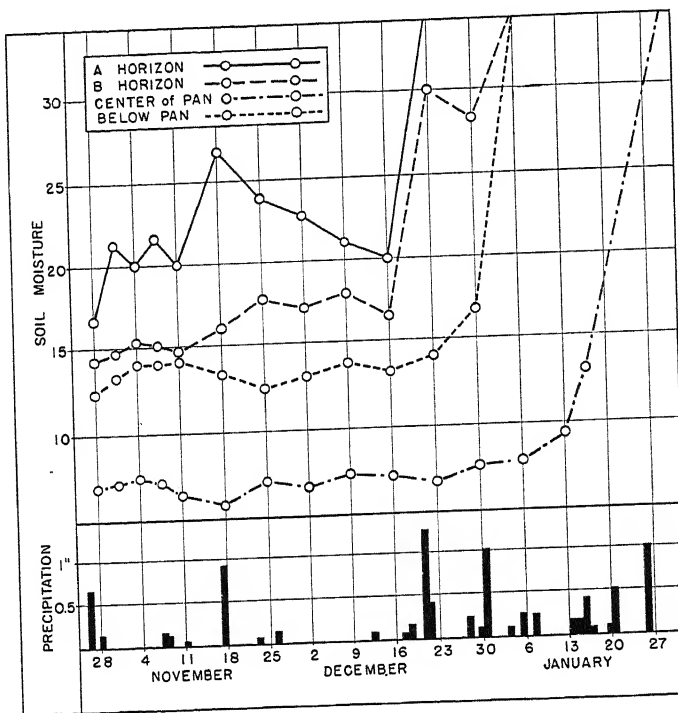


FIG. 9. RUN OF MOISTURE CONTENT THROUGH NOVEMBER 1946 TO FEBRUARY 1947 IN THE DIFFERENT HORIZONS OF LEONARDTOWN SILT LOAM

Field recording and determination by E. F. Miles

and is subject to the least fluctuation. The moisture content in the soil both above and below the pan is always higher than that of the pan. It will be noted that toward the end of the period under observation, all horizons including the hardpan became saturated. A thorough saturation of the undisturbed hardpan, however, is rather doubtful, and the measurement results shown in figure 9 might be due to several factors. First, it cannot be ascertained at present whether the elements installed in the hardpan are within the massive blocks of the pan or in the clay-filled crack through which water may penetrate the pan without saturating the blocks. Second, the pit was flooded several times and sometimes for prolonged periods so that water could penetrate the pan along

the cleavages laterally as well as vertically from its surface. Third, water could reach the elements along the cables and borings through which the elements were installed. It must be pointed out, also, that all elements were calibrated with the surface soil and that the recalibration with materials of the respective horizons at the end of measurements might result in some changes in the character of the curves. For the present, therefore, the authors feel that further discussion of these data would not be justified.

#### GENERAL DISCUSSION

Marbut (see footnote 5) wrote as follows:

In the coastal-plain region, near Washington, D. C., certain remnants of an old smooth land surface, antedating the inauguration of the existing cycle of erosion, are still intact. A soil, Leonardtown silt loam, has developed on these areas under the influence of a ground water surface lying, it seems, at about 3 feet beneath the surface of the ground. An indurated layer has developed at this level . . . The A and B horizons . . . are normal A and B Podzolic horizons but the lower part of or below the B an indurated layer has higher silica content than the A and considerably higher than in B and C . . . It is possible that the induration is due to cementation by silica but that has not yet been definitely proved . . . The sa [silica to alumina] ratio for B<sub>2</sub> [the hardpan] is exceptionally high. This is caused by the high percentage of SiO<sub>2</sub> as well as low percentage of Al<sub>2</sub>O<sub>3</sub> in this horizon . . . In this case there can be no question that the induration is accompanied by accumulation of silica.

In making this statement, Marbut apparently did not consider that by far the greater part of the silica in this soil is in the form of quartz, the content of which in the hardpan might be considerably higher than in the other soil horizons. Therefore, a higher content of silica in the pan may be due, not to the accumulation of silica in this layer, but to the difference in source and mineralogical composition of the parent materials from which the hardpan and the other soil horizons were developed.

Our data tend to rule out any cementation of this hardpan, and especially cementation by silica. The data in table 1 show that pH throughout the soil profile ranges from only 5.1 to 4.1. Under this acid condition any movement of free silica is hardly feasible. Marbut points out that the A and B horizons of the Leonardtown soil are normal A and B horizons of a podzolic soil in which a relative increase of the silica content normally takes place in the A<sub>2</sub> horizon because of removal of the sesquioxides.

Furthermore, Marbut suggests a possibility that the hardpan developed under the influence of a high ground-water level, which also is difficult, if not impossible, to prove. To begin with, such a development naturally would be accompanied by a strong gleyization of the material below the water table, which was not observed in any deep exposure of this soil. Again, in poorly drained areas on the flats occupied by the Leonardtown soils, in which the water table is high, the hardpan is conspicuously absent.

Winters<sup>8</sup> described several soils having hardpans similar to that of Leonard-

<sup>8</sup> Winters, E. 1942 Silica hardpan development in the red and yellow podsolc soil region. *Soil Sci. Soc. Amer. Proc.* 7: 437-440.

town silt loam and agreed with Marbut's suggestion about the possibility of its cementation by silica. Winters suggested that such a cementation could result from precipitation and dehydration, during drought periods, of soluble silica liberated by hydrolysis of silicates. He admitted, however, that his conclusion was based on indirect evidence and presented no data to support his hypothesis except for consideration of relationships of the pan to the environmental condition.

Somewhat similar hardpan in certain soils of the Ozark Region was described by Krusekopf<sup>9</sup>, who also assumed that this hardpan is cemented by silica. Krusekopf presented no analytical data supporting his conclusion. The parent material of the Ozark soils, however, is different from that of the Coastal Plain soils.

More recently Smith and Browning<sup>10</sup> made an interesting study of some physical and chemical properties of the hardpan or "siltpan" in various soils of West Virginia. These appear to be essentially similar to the pan in Leonardtown silt loam. Smith and Browning concluded that "silt pans in West Virginia are apparently never strongly cemented layers," their firmness being due "to the high density of packing and the complete lack of any effective aggregation." This conclusion is fully supported by the data presented in this paper.

The data, especially on mechanical and mineralogical composition of the various horizons of Leonardtown silt loam, lead to the conclusion that the hardpan and the upper horizons of this soil are developed from different materials. The material of the hardpan is rather heterogeneous in mechanical composition, whereas the material above the pan consists largely of silt and sometimes is referred to as loess-like. Such a stratification may or may not be characteristic of the gravel-free cover throughout the remnants of the Pleistocene terraces of the Coastal Plain. Thickness and texture of the upper layer vary from place to place, and in some areas such a layer may be absent entirely, giving rise to the different types of the Leonardtown series or to soils of an entirely different series. The condition which we describe is typical only of the areas occupied by the silt loams of the Leonardtown series.

A difference in the origin of the parent materials of the hardpan and the upper horizons of the soil does not necessarily imply that the lower layer could not be hardened as a result of development of the existing soil. Its hardness might be either an original characteristic of the lower layer or a secondary characteristic acquired after deposition of the new material above this layer.

A secondary induration of the hardpan can be produced by impregnation of the originally loose material with some binding substance, such as iron oxide or free silica, which would irreversibly solidify in this horizon, or by infiltration of colloidal clay, which would clog at least the largest voids and render the pan almost impermeable. Neither of these processes applies in this case. These

<sup>9</sup> Krusekopf, H. H. 1942 The hardpan soils of the Ozark Region. *Soil Sci. Soc. Amer. Proc.* 7: 434-436.

<sup>10</sup> Smith, R. M., and Browning, D. R. 1946 Occurrence, nature, and land-use significance of "siltpan" subsoils in West Virginia. *Soil Sci.* 62: 307-317.

pan are uncemented and their clay content usually is lower than that in the B horizon above the pan and in material beneath the pan. Thus, it appears that the induration of the pan is an original rather than a secondary characteristic developed because of the close packing of particles during their deposition and before the accumulation of the silty material on the surface of the pan, that is, well before development of the Leonardtown soil began.

Because of texture and evidence of stratification it is certain that the pan material is water-transported. The same may or may not be true of the silty material of the upper layer; the latter or at least a part of it could well have been assorted and spread by wind. Whether deposited by wind or water, the differences between the texture and mineralogical composition of the pan and the upper horizons indicate that there must have been a marked change in conditions under which these materials were laid down.

It seems possible that accumulation of the latest sediments did not begin immediately after sedimentation of the underlying material ended. Perhaps there was an interval, however short, between the end of sedimentation of the pan material and the beginning of accumulation of the silty mantle. During this interval the pan material could undergo certain changes and rather strong cracking. The general pattern and character of the polygonal cleavages of the hardpan very much resembles mud cracks filled with almost pure clay. Development of these cracks hardly would be possible during accumulation of the pan material because every new sheet of sediment would tend to obliterate the previously formed cleavages and fill them with the unassorted material. The cracks are as wide as an inch at the top of the pan and gradually narrow to the vanishing point at the depth of the pan. The laminated structure of the filling material, pointed out in reference to *E* and *F* in figure 8, seems to indicate that filling took place when cracking broke the whole layer from top to bottom into the roughly polygonal blocks.

Cracking and filling of the cracks presumably were completed before accumulation of the silty sediments on the surface of the pan began, because the cleavages conspicuously begin from the top of the hardpan just beneath the platy layer and do not extend upward into the clayey B horizon, and the filling material in cracks does not contain appreciable quantities of silt. These considerations lead to the conjecture that the surface of the pan might have been stabilized for a certain time before it was buried under the most recent sediments. Cracking of the lower soil horizons without any cracking of the upper ones usually takes place only if the lower horizons have a much higher clay content than the upper; this is quite opposite to the distribution of clay in the Leonardtown soil.

The walls of cracks formed by the vertical facets of the polygonal blocks of the hardpan are strongly bleached from top to bottom. Bleaching extends laterally into the body of the blocks for more than 1 inch at the mouths of the cracks and just a few millimeters at their ends near the base of the hardpan. Beyond the bleached zone there is a rusty yellow zone brightly colored by iron oxides. Thus, it appears that the walls of the cracks were affected by weathering, at least to the extent of redistribution of iron oxides and certain changes in

their state of oxidation, although the exact nature of these changes cannot be ascertained at this time.

Mud cracks develop as a result of shrinkage of clay and silt on drying. The clay content of the pan material, however, is so low that it is doubtful whether such a material could shrink sufficiently to produce these cracks, although a sample of thoroughly crushed and puddled pan material split when allowed to dry in a large beaker. Perhaps the initial splitting of the sediments in the field produced smaller cracks which could have been enlarged later by frost action. A mere film of water in the cleavage should press on the walls on freezing and expand the crack. During the summer such a slightly widened and reinforced crack could have been filled with clay, which would dry and shrink, allowing more water to enter the same crack, to freeze, and further to widen the crack. The pattern of polygonal cleavage of the pan resembles the pattern of frost cracking of the soils in Tundra. It was found that the surface of Tundra breaks in winter into polygonal, mostly hexagonal, blocks ranging in size "from the size of a plate to that of a wagon wheel" (Berg, Liverovskiy, and others).

If frost action had any influence on the development of these cracks, then it might have been a contributing factor in the compaction of the pan material. The average diameter of the polygons is about 2 feet. Most blocks are broken by secondary smaller cracks. Being surrounded by large cracks and subject to considerable pressure from freezing water on all sides, the blocks gradually could be more and more compressed and compacted. The cracking, regardless of its origin and development, contributed to the reduction in volume and increased density of the pan.

It has already been mentioned that deposition of the pan material and development of the pan could take place under conditions different from those under which the silty sediments were laid down. It is not inferred, however, that former conditions were similar to those of the Tundra regions, but the possibility of winters being colder, allowing freezing of soils to the depth of a foot or two, should not be ruled out.

The reasoning presented in this discussion leads us to the conclusion that formation of the Leonardtown hardpan antedated deposition of the sediments from which subsequently the upper horizons of this soil were developed.

#### SUMMARY

Leonardtown silt loam occupies relatively flat, undissected remnants of several Pleistocene terraces in the Coastal Plain. These terraces are built of poorly stratified gravelly sediments covered with a mantle of more recent gravel-free material. There are indications that before being covered, the older sediments might have been slightly laterized.

The entire profile of the Leonardtown soil developed from recent mantle. These sediments consist of two layers: The lower, of a rather coarse and heterogeneous texture, and the upper, having a loess-like character. The former was laid down by water, whereas the latter might have been spread by either water



or wind. There is a rather abrupt boundary between these layers, which coincides with the surface of the hardpan.

The lower part of the profile of the Leonardtown soil consists of uncemented "physical" hardpan. This hardpan is not a true soil horizon, being formed from the lower part of the mantle before this was covered by the loess-like sediments from which the A and B horizons of Leonardtown silt loam were developed. The hardness of this pan is largely due to the dense packing of its primary particles.



## APPARENT SPECIFIC VOLUME AND SHRINKAGE CHARACTERISTICS OF SOIL MATERIALS<sup>1</sup>

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The change in apparent specific volume<sup>3</sup>, or the swelling and shrinkage which accompany wetting and drying, is an important property of soil, since it is by this process that soils, particularly clay soils, are physically reconditioned. Cracking, which occurs upon drying, increases the capability of the soil to absorb water and to exchange gases with the atmosphere. Subsequent wetting causes the soil to swell. Swelling, because of the entrapped air and the heterogeneous nature of the wetting process, causes the larger structural units of the soil mass to break apart. This increases the porosity and improves the tilth. The character of shrinkage as it occurs progressively throughout the moisture range may or may not be immediately applicable. Since, however, it further characterizes the properties of soil, it may furnish a basis for differentiating soils with greater precision and may possibly offer a partial explanation for the different behavior of soils of different textures, clay mineral content, and different absorbed ions.

The process of swelling and shrinking, which accompanies changes in soil moisture, likewise is important from an engineering standpoint in that the magnitude of the volume changes determines, to a large degree, the suitability of soil material for construction purposes. Foundation design is influenced by the nature of site materials, and the size of reservoirs and other structures for storing and conveying water depends on watershed yield and runoff characteristics. These, in turn, depend upon the capacity of land surfaces to take up and store water, which is, in part, determined by the soil properties reflected in volume change relationships.

### REVIEW OF LITERATURE

Considerable attention has been given to investigation of the process involved in volume changes accompanying the drying of soil. Shrinkage, as it is associated with plastic blocks prepared by kneading soil at a moisture content near the sticky point, has been shown by Haines (3) to take place in two stages. The first stage is characterized by a change in volume of the soil mass just equal to the volume of the water removed as the soil dries. Shrinkage of this character is termed "*normal shrinkage*" and is confined roughly to the moisture range be-

<sup>1</sup> Contribution from the U. S. Department of Agriculture, Soil Conservation Service, and the Utah Agricultural Experiment Station, Logan, Utah.

<sup>2</sup> Soil technologist, Soil Conservation Service. The assistance rendered by Miss LaRee Lamb, Soil Conservation Service, in connection with measurements and computations; and by James P. Thorne, Soil Conservation Service, in performing certain chemical analyses is gratefully acknowledged.

<sup>3</sup> The apparent specific volume is the volume occupied by unit weight of soil.

tween field capacity and the wilting percentage. As the moisture content is further reduced, air begins to replace part of the water removed, and the shrinkage accompanying drying corresponds to an increasingly smaller fractional part of the water lost by evaporation. This second stage is termed *residual shrinkage*. Haines attributed residual shrinkage to colloidal coatings on the soil particles and demonstrated that it could be produced in blocks of kaolin (a clay mineral in which residual shrinkage is otherwise absent) by precipitating silica gel on kaolin in suspension.

The findings of Grimm (1), Hendricks (2), Kelley (4), Ross and Hendricks (7), and others, have demonstrated that clays have definite molecular structure, and have indicated that swelling of clays results from absorption of water between the silicate layers of the mineral. The entrance of water causes the spacing between the planes parallel to the surface to increase, while lateral dimensions remain constant. The fact that the degree of swelling differs in clay minerals suggests that the shrinkage which accompanies the drying of soil is related to

TABLE 1

*Relation between water content and cleavage spacing in montmorillonite according to Hofmann and Bilke*

H <sub>2</sub> O PER 100 GM. WATER-FREE SUBSTANCE	SPACING OF CLEAVAGE PLANE
gm.	A.
10.0	11.25
13.9	12.1
19.5	13.4
24.2	14.6
29.5	15.1
36.3	15.6
41.8	15.7
59.0	17.8

the character of the clay component or admixture of clay minerals constituting the clay fraction of the soil. The relation between water content and cleavage spacing in calcium montmorillonite (table 1), as shown by the results of Hofmann and Bilke [from Ross and Hendricks (7)], indicates that the change in lattice spacing with change in moisture content might result in a considerable change in volume of the soil mass. The results of Hofmann and Bilke indicate also an essentially uniform change in cleavage spacing as the absorbed water increases. The amount of water taken up by montmorillonite over a range of relative humidities is reported to be the same whether the exchangeable ion is Na<sup>+</sup>, H<sup>+</sup>, or Ca<sup>++</sup>. The cleavage spacing, however, was found to vary widely with the exchangeable ion on the montmorillonite, being greater and about the same for Ca<sup>++</sup> and H<sup>+</sup>, and smaller for Na<sup>+</sup>. On the contrary, Bradley, according to Grimm and Clark [Ross and Hendricks (7)], found that the cleavage did not increase uniformly but rather increased in stages as definite hydrates containing one, two, or three layers of water molecules. Present information is not adequate to indicate the true manner in which hydration takes place. It might be ob-

served, however, that the moisture range over which Hofmann and Bilke measured the lattice spacing appears to be in the range of normal shrinkage, and it is possible, if measurements were continued into the drier range, that the relationship would not hold.

It would seem that the fact that kaolin has a nonexpanding lattice whereas the lattice structure of montmorillonite is of the expanding type, according to Grimm (1) and others, offers a better explanation than the colloidal coating theory for the difference in the shrinkage characteristics of kaolin and the clays studied by Haines. Assume that the soil mass is composed in part of clay having a lattice structure of the expanding type. It is highly probable, then, that as the water content is depleted to a point where the soil particles are in intimate contact, further depletion in moisture content may be at the expense of both capillary or film water and of water held in the lattice structure. If it can be assumed that the water in the lattice structure is held with a greater force than that exerted by capillary attraction, a disproportionately larger amount of film water could be removed, with air or water vapor occupying the pore space emptied. Thus, by this process of reasoning, we have provided for shrinkage of the type which has been termed *residual shrinkage*. Should material possessing the expanding lattice structure be absent, as in the case of kaolin, residual shrinkage would be absent, because there would be no further opportunity for contraction once the particles of the material had come in contact with one another.

Shrinkage characteristics have been found by Lauritzen and Stewart (5) to vary with the soil used and its apparent specific volume. Clods<sup>4</sup> obtained from a profile of Houston black clay from the surface to depths of 6 feet exhibited a progressive decrease in apparent specific volume with depth. The rate of decrease was not uniform but decreased with depth, indicating that a condition approximating maximum compaction of the material was being approached. It was observed, also, that as the apparent specific volume of the material decreased, the character of the shrinkage curve more nearly resembled that exhibited by plastic blocks. This seemed to suggest a relationship between the character of the pore space within the soil mass and the shrinkage which accompanies drying. The difference in the shrinkage characteristics of Houston black clay and Crockett fine sandy loam tends to support this suggestion.

#### EXPERIMENTAL PROCEDURE AND MATERIALS

The objective of this investigation was to determine the influence of texture and structure on the shrinkage characteristics of soil materials. Two soils, Houston black clay and Oasis silt loam, widely separated geographically and of markedly different physical properties, were selected for study and comparison. Along with shrinkage measurements on these soils and on soil-sand mixtures of these soils, shrinkage measurements were made on mixtures of two clay fractions from each of these soils and sand and on mixtures of these soils and alfalfa meal.

<sup>4</sup> The term *clod* as used in this paper, refers to a random segment of the soil mass in which the natural structure has not been modified. It does not imply a fragment of cemented material or material of above average density.



Separation of the clay fractions for study was designed to avoid the possibility of textural size classes masking each other's influence. The alfalfa meal mixtures were included in an effort to provide a material which would differ chiefly in its porosity characteristics. To determine the influence of structure on shrinkage, identical materials in the form of blocks and clods were subjected to shrinkage measurements as they dried, the assumption being that structure was largely destroyed by the kneading which was employed in the preparation of the plastic blocks and that some structure existed in the clods.

The volume of the blocks and clods ranged from 5 to 15 cc., the blocks normally being about 10 cc. in volume and the volume of the clods ranging more widely, the size of the clods being governed to some extent by the size of units which could readily be broken from the wet soil mass with a minimum of disturbance. Blocks were prepared from air-dry soil brought to a moisture content near the sticky point by the addition of water. After the water was added the soil was thoroughly kneaded by hand, following which blocks in the form of cubes were moulded by hand with the aid of a spatula. The change in weight and volume of plastic blocks and clods as they dried was determined at intervals corresponding to a reduction in moisture content of 1 to 3 per cent. The blocks or clods, as the case may be, were coated with a thin layer of paraffin, and the volume was determined by the water displacement method in accordance with the procedure described elsewhere by Lauritzen and Stewart (5).

The  $<0.002$ - and  $0.005$ - $0.002$ -mm. clay fractions used in the clay-sand mixtures were separated from the soil as follows: Fifty grams of soil was stirred for 10 minutes with a Bouyoucos stirrer in approximately 300 ml. of water to which 5 ml. of  $N$  NaOH was added. Each 50 gm. of soil after dispersion was made up to a volume of 1050 ml. Nineteen separate dispersions prepared in this manner were poured into a stone crock and constituted a sample from which the clay fractions were recovered by siphoning off the upper 20 cm. of a suspension 32 cm. in depth and passing the suspension through a Sharples supercentrifuge. The principle stated in Stoke's law was employed in making the separation. The time of settling for the two clay fractions was as follows:  $<0.002$ -mm. clay, 16 hours;  $0.002$ - $0.005$ -mm. clay, 2 hours and 20 minutes. The water coming through the centrifuge was caught and returned to the crock, the suspension stirred, allowed to settle, siphoned, and centrifuged again. This was repeated five times for the 16-hour settling time and four times for the 2-hour-and-20-minute time. The amount of material recovered after successive siphonings and centrifuging is shown in table 2. When the mechanical analysis of the two soils is considered, it is apparent that the method of separation resulted in recovery of disproportionate amounts of the respective fractions. The  $<0.002$ -mm. fraction recovered from Houston black clay was 67 per cent of the amount present, and that from the Oasis silt loam was 122 per cent. Apparently some of the textural fraction larger than 0.002 mm. was included in the 0.002 clay separation from Oasis silt loam, whereas only a part of the 0.002-mm. clay in Houston black clay was recovered. This may be explained in part by the difference in the ease with which the two soils are dispersed and the fact that Oasis silt loam contained

28 per cent of 0.005–0.002-mm. clay, whereas Houston black clay contained only 18 per cent of this clay fraction. The temperatures at the time settling began and just prior to siphoning were recorded; however, no correction was made for the settling time, although the temperature in the laboratory was subject to some fluctuation. The sand used in the soil-sand and clay-sand mixtures was pure quartz sand, diameter 0.25 to 0.15 mm. The mixtures were prepared by adding the required amount of sand to the air-dried ground clay separate.

The clods of the 0.002-mm. clay and clay-sand mixtures were obtained from samples subjected to the following treatment: The material was mixed, placed in cans with holes in the bottom to provide drainage and left for a 2-year period, during which time the mixtures were cropped twice to wheat and once to alfalfa, as a means of increasing porosity and promoting structural development. After the first crop of wheat the soil columns were inverted in the cans. Preparatory to making shrinkage measurements the soil was saturated by placing the cans

TABLE 2  
*Clay recovered from suspension by successive centrifugings*

RUN NO.	HOUSTON BLACK CLAY		OASIS SILT LOAM	
	<0.002 mm.	0.005–0.002 mm.	<0.002 mm.	0.005–0.002 mm.
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
1	30	46	59	40
2	16	22	33	20
3	12	16	14	12
4	6	9	10	7
5	3		6	
Total . . . . .	67	93	122	79

containing the air-dry soil material in dishes of shallow water. After they had soaked several days, the water was increased to a depth slightly greater than the height of the soil column. The cans were then removed from the water and allowed to drain overnight. Segments of the soil referred to as *clods* were obtained by breaking out sections from the soil mass. Samples of this same material were used in the preparation of plastic blocks.

Alfalfa meal was added to Houston black clay and Oasis silt loam in the following proportions<sup>5</sup> to obtain an indication of the influence of added porosity on shrinkage: 1. Soil 2 parts + alfalfa 1 part; 2. Soil 4 parts + alfalfa 1 part; 3. Soil 8 parts + alfalfa 1 part. The additions were made in November, 1942. The mixtures were then watered from time to time to promote decomposition and incorporation of the material, ground and mixed again, and returned to original glass jar containers and watered at intervals. Distilled water was used to avoid addition of salts. Wheat was planted but germinated in only the two lowest concentrations of organic matter with Houston black clay and in only

<sup>5</sup> The quantity of soil is expressed on the basis of soil material dried to constant weight at 110° C., and the organic matter on the basis of alfalfa meal dried to constant weight at 65° C.

the lowest with Oasis silt loam. Drainage probably should have been provided to allow removal of the toxic products of decomposition and to promote better incorporation of the organic matter. Later, red clover was planted. A partial stand and some growth were obtained on all mixtures, though these were poor on the mixtures containing the largest quantities of alfalfa, particularly in the case of Oasis silt loam.

Houston black clay is a highly calcareous soil. Oasis silt loam is also calcareous but contains, in addition, sodium salts. The textural composition, salt content, base-exchange capacity, exchangeable sodium, and pH of these two soils and one other soil, for which shrinkage and apparent specific volume measurements are reported, are given in table 3. The mechanical analyses were made

TABLE 3  
*Some physical and chemical properties of soils for which shrinkage and dry specific volume are reported*

	HOUSTON BLACK CLAY	OASIS SILT LOAM	SALT LAKE SILT LOAM
Sand 2.0-0.05 mm..... per cent	9	8	7
Silt 0.05-0.002 mm..... per cent	40	66	69
Clay <0.002 mm..... per cent	51	26	24
Clay <0.005 mm..... per cent	69	54	50
Dispersion..... per cent	10	22	14
Total soluble salt..... per cent	<0.5	<0.5	<0.5
Calcium*..... e.p.m.	15.9	5.7	11.0
Magnesium*..... e.p.m.	0.8	4.7	7.7
Sodium*..... e.p.m.	0.9	21.4	4.4
Base-exchange capacity..... m.e./100 gm.	35.5	18.1	29.7
Exchangeable sodium..... per cent	0.6	7.8	0
pH.....	7.8	8.1	7.5

\* 1:5 soil-water extract.

in accordance with a modification of the method specified by the American Society for Testing Materials—Designation D422. Dispersion was determined by the method of Volk (9). Total salts and the concentration of calcium, magnesium, and sodium were determined on 1:5 soil-water extract. Calcium was determined by titration of the oxalate with potassium permanganate; magnesium, gravimetrically as the pyrophosphate; and sodium, gravimetrically as sodium uranyl acetate. The base-exchange capacity was determined by saturation with ammonium acetate and subsequent distillation and titration of the absorbed ammonia. Exchangeable sodium is the sodium determined on the ammonium acetate leachate. The pH is that of the soil paste as determined with a glass electrode. Oasis silt loam, unlike the other soils, contains an appreciable amount of exchangeable sodium. It has about half the base-exchange capacity of Houston black clay and about the same textural composition as Salt Lake silt loam. Salt Lake silt loam, however, is intermediate in base-exchange capacity and contains no exchangeable sodium.

## RESULTS

The moisture range over which shrinkage occurred was narrowed by adding sand to clay through its effectiveness in reducing the water-holding capacity of the material. The moisture range over which normal shrinkage occurred became progressively narrower as the sand content increased and markedly narrower for corresponding mixtures of Oasis silt loam than for Houston black clay (figs. 1, 2, 3, 4, 7, 8, 9, and 10). Remembering that *normal shrinkage* has been defined as shrinkage in which the change in volume of the soil mass is just equal to the volume of water lost, we see that the addition of sand tended to eliminate normal shrinkage. An apparent specific volume relationship defining a line 45 degrees with the abscissa in figures 1 to 6 and a volume change ratio of unity in figures 7 to 12 is indicative of normal shrinkage. Some normal shrinkage was exhibited, however, by blocks<sup>6</sup> of all 0.002-mm. Houston black clay and 0.002-mm. Houston black clay-sand mixtures. The addition of sand, on the other hand, to the 0.002-mm. clay fraction of Oasis silt loam largely eliminated normal shrinkage in blocks, as shown by the length and slope of the line indicated by the points plotted in figures 3 and 8. Substitution of 0.005-mm. for 0.002-mm. clay greatly reduced the range of normal shrinkage for Houston black clay blocks and resulted in elimination of normal shrinkage in all blocks prepared of the 0.005 clay from Oasis silt loam (fig. 4). It will be seen that even in the absence of sand the 0.005-mm. Oasis silt loam failed to exhibit normal shrinkage even over a narrow moisture range (fig. 4). The term *normal shrinkage* hardly applies to clods. Sand in quantities of 25 per cent or more, however, resulted in elimination of a moisture range in which the reduction in volume is equal to the volume of the water lost (figs. 2, 3, 9, and 10). The extent to which water was replaced by air as the clods dried increased with the sand content. Where sand was added to the whole soil the result was similar in both blocks and clods to that in which a larger quantity was mixed with the clay separate. This is as would be expected, since the soil contains some sand and silt before the addition is made.

The presence of sand did not influence the apparent specific volume of blocks prepared of Houston black clay soil-sand mixtures or 0.002-mm. Houston black clay-sand mixtures (figs. 1 and 2). In the blocks prepared of the 0.002-mm. fraction from Oasis silt loam and sand, however, (fig. 3) the apparent specific volume became progressively smaller as the sand content increased, the departure or difference in the apparent specific volume increasing as the moisture decreased, the dry specific volume for the clay alone being approximately 0.54, the 25 per cent sand 0.52, and the 50 per cent sand 0.50. The same relationship was found for clods of the 0.002-mm. clay fraction of Oasis silt loam (fig. 3) except that the departure was fairly uniform throughout the moisture range. Increased quantities of sand increased the specific volume of the dry clods of the 0.002-mm. Houston black clay (fig. 2), the reverse of the situation exhibited by Oasis blocks and clods. The apparent specific volume of Houston black clay

<sup>6</sup> The term *block* as used in this paper is synonymous with *plastic block*.

blocks, as previously mentioned, was not influenced by the sand content. The apparent specific volume of blocks representing the 0.005-0.002 mm. fraction was affected in much the same way by the addition of sand as were the blocks of 0.002-mm. clay, the specific volume decreasing with increasing sand content for Oasis silt loam and changing little, if at all, for Houston black clay (fig. 4).

Addition of organic matter in the form of alfalfa meal increased the apparent specific volume, particularly the dry apparent specific volume of blocks and clods,

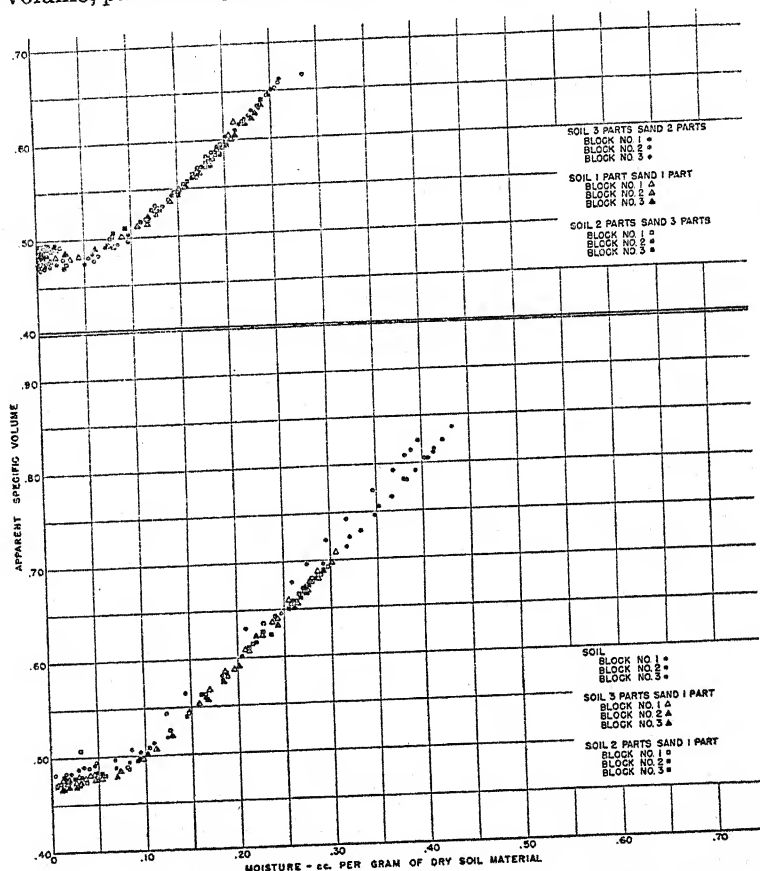


FIG. 1. CHANGE IN APPARENT SPECIFIC VOLUME OF PLASTIC BLOCKS WITH CHANGE IN MOISTURE CONTENT FOR HOUSTON BLACK CLAY AND HOUSTON BLACK CLAY-SAND MIXTURES

with the exception of blocks of Oasis silt loam where the low organic matter blocks had the largest apparent specific volume (figs. 5 and 6). It eliminated normal shrinkage in blocks of Oasis silt loam and in the high organic matter mixture of Houston black clay (fig. 12) and, like sand, increased the fractional part of the water replaced by air in clods as they dried (fig. 12).

The volume change ratio,  $\frac{\text{change in volume}}{\text{change in weight}}$ , is the change in volume of the



soil mass accompanying loss of an increment of water divided by the volume of the water lost. It is a measure of the extent to which shrinkage is accompanied by the loss of an equivalent volume of water or the extent to which the water lost is replaced by air as the soil dries. This ratio has been plotted against moisture content in figures 7 to 12. The individual ratio determinations for the  $<0.002$ -mm. clay and clay-sand mixtures are plotted in figures 7 to 10, and summary curves for these together with the  $0.005$ - $0.002$ -mm. clay and soil-alfalfa meal mixtures in figures 11 and 12. These graphs show some variation between individual blocks and clods of the same material and also some deviation between

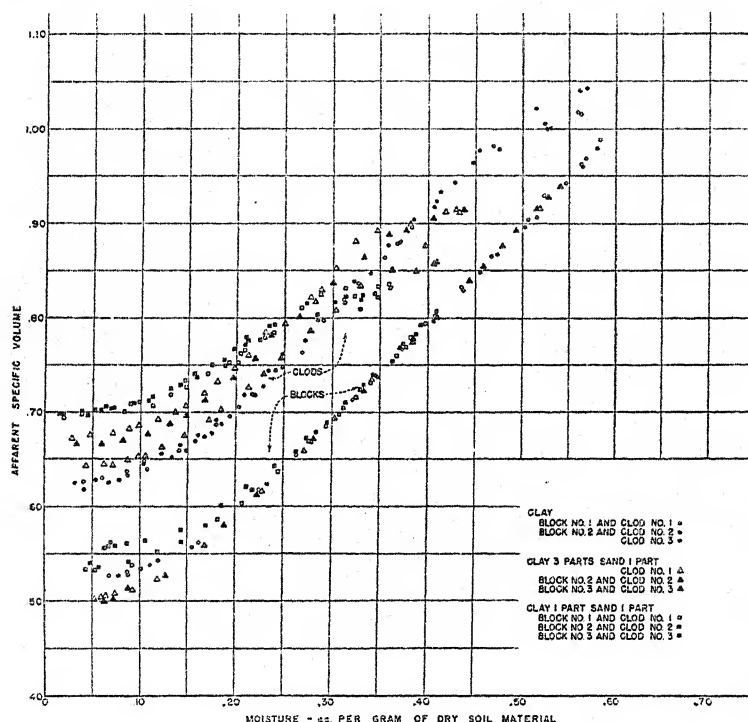


FIG. 2. CHANGE IN APPARENT SPECIFIC VOLUME OF PLASTIC BLOCKS AND CLODS WITH CHANGE IN MOISTURE CONTENT FOR THE  $<0.002$ -MM. CLAY FRACTION OF HOUSTON BLACK CLAY AND  $<0.002$  MM. CLAY-SAND MIXTURES

individual determinations and the general form which the shrinkage takes. It is evident, however, that the character of the shrinkage associated with blocks and clods is different and that sand content and organic matter influence this characteristic. The influence of these components has already been mentioned in connection with figures 1 to 6. Figures 7 to 12, however, emphasize the influence of sand and organic matter and the source of the clay component on the distribution of air and water in the soil mass as it dries. Occasionally the volume change ratio is found to deviate widely from the general trend. This was more common in clods than in blocks and was characteristic of clods of the highly

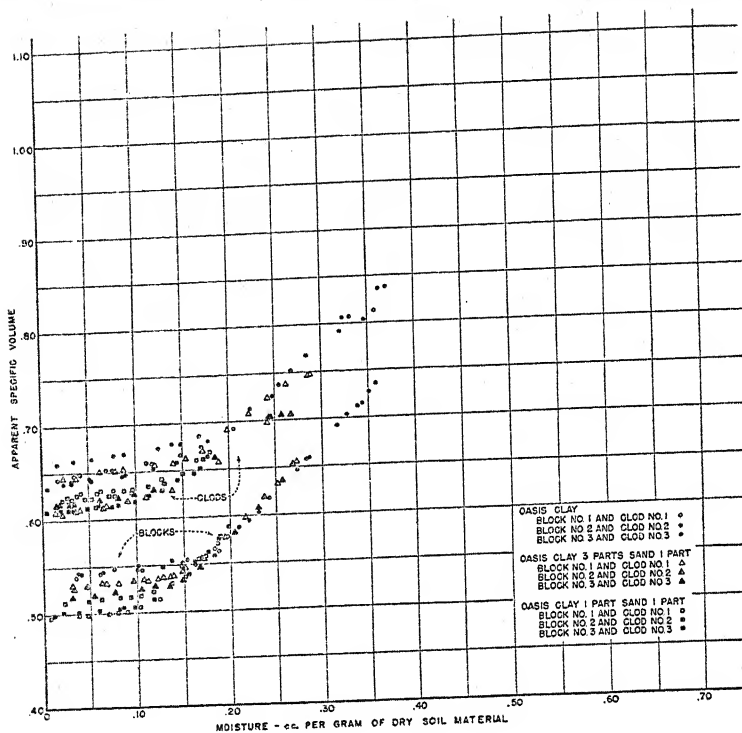


FIG. 3. CHANGE IN APPARENT SPECIFIC VOLUME OF PLASTIC BLOCKS AND CLODS WITH CHANGE IN MOISTURE CONTENT FOR THE  $<0.002$ -MM. FRACTION OF OASIS SILT LOAM AND  $<0.002$ -MM. CLAY-SAND MIXTURES

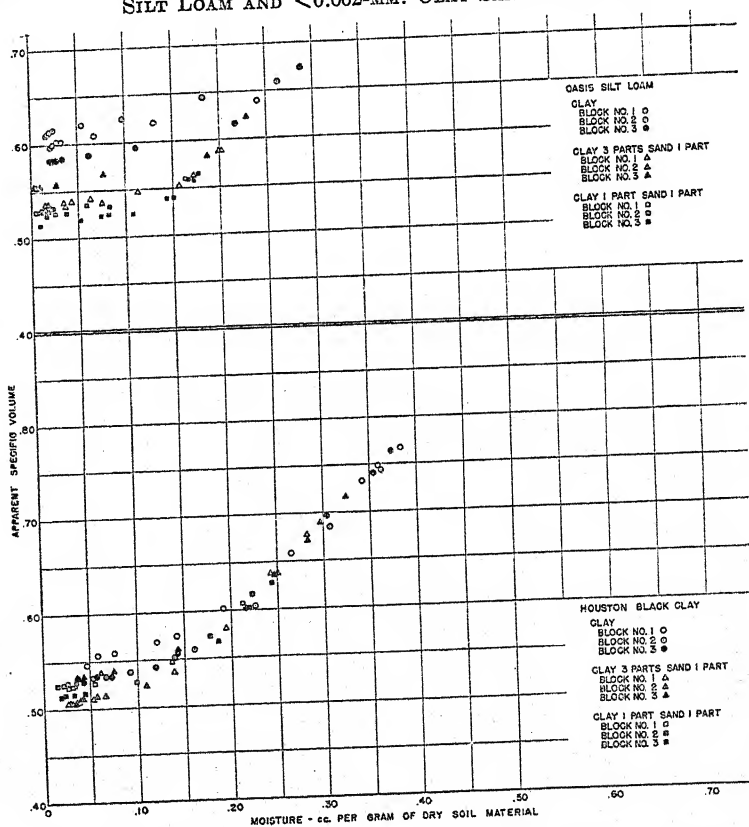


FIG. 4. CHANGE IN APPARENT SPECIFIC VOLUME OF PLASTIC BLOCKS WITH CHANGE IN MOISTURE CONTENT FOR THE  $0.005$ - $0.002$ -MM. CLAY FRACTION AND SAND MIXTURES OF THIS CLAY FRACTION

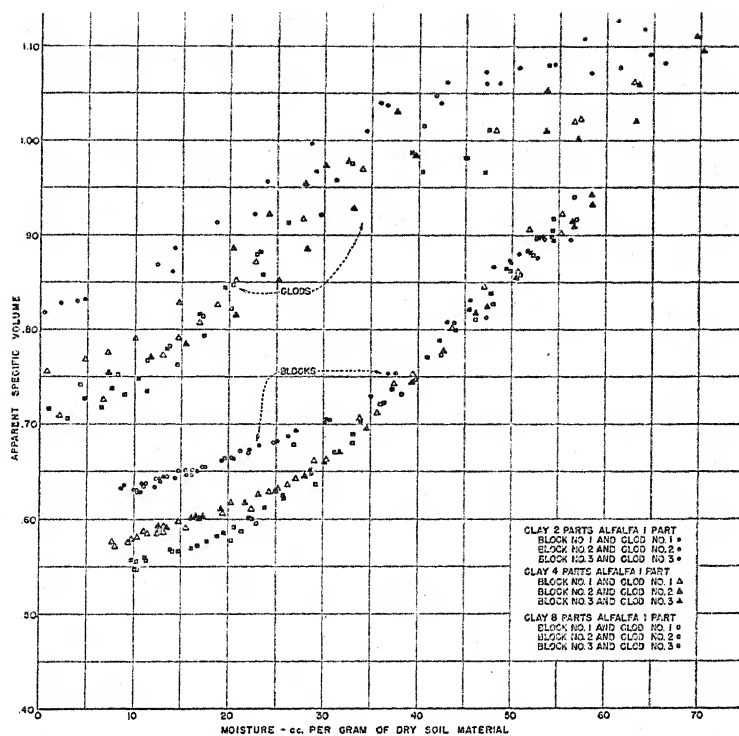


FIG. 5. CHANGE IN APPARENT SPECIFIC VOLUME OF PLASTIC BLOCKS AND CLODS WITH CHANGE IN MOISTURE CONTENT FOR HOUSTON BLACK CLAY-ALFALFA MIXTURES

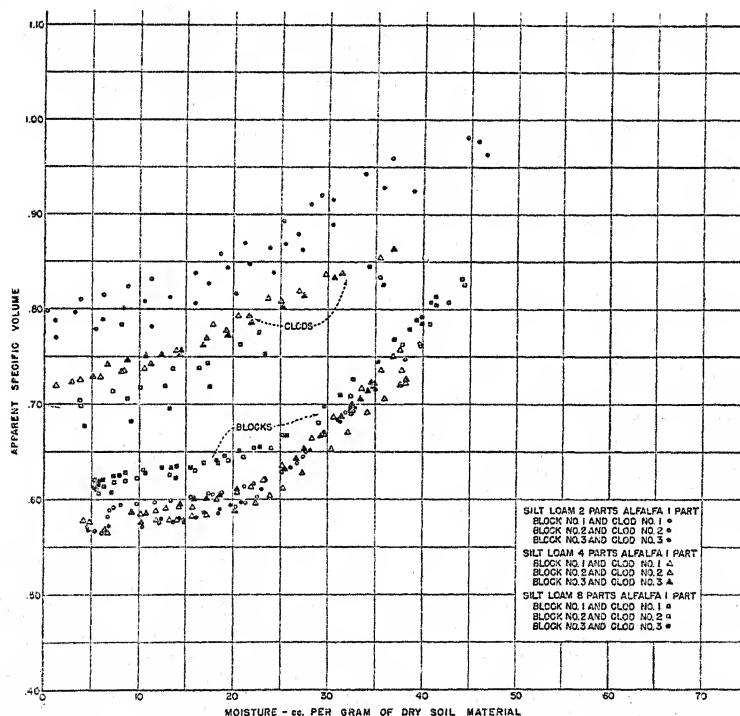


FIG. 6. CHANGE IN APPARENT SPECIFIC VOLUME OF PLASTIC BLOCKS AND CLODS WITH CHANGE IN MOISTURE CONTENT FOR OASIS SILT LOAM-ALFALFA MIXTURES

porous soil-alfalfa meal mixtures. It was common for the ratio to be greater than unity in the high moisture range and also in the region of the maximum ratio

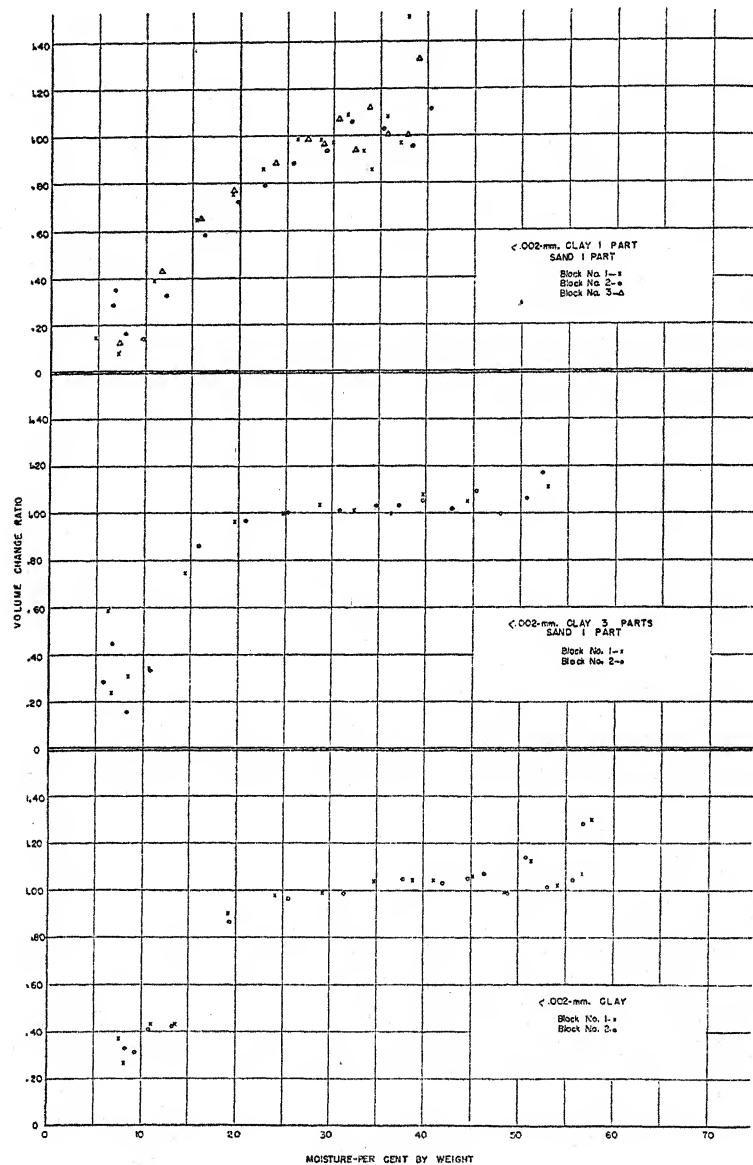


FIG. 7. VOLUME CHANGE RATIO FOR PLASTIC BLOCKS PREPARED OF THE <0.002-MM. CLAY FRACTION FROM HOUSTON BLACK CLAY AND <0.002-MM. CLAY-SAND MIXTURES

for the 0.002-mm. Houston black clay clods. There was also a tendency for the ratio to increase slightly in the dry extreme of the shrinkage range, as indi-

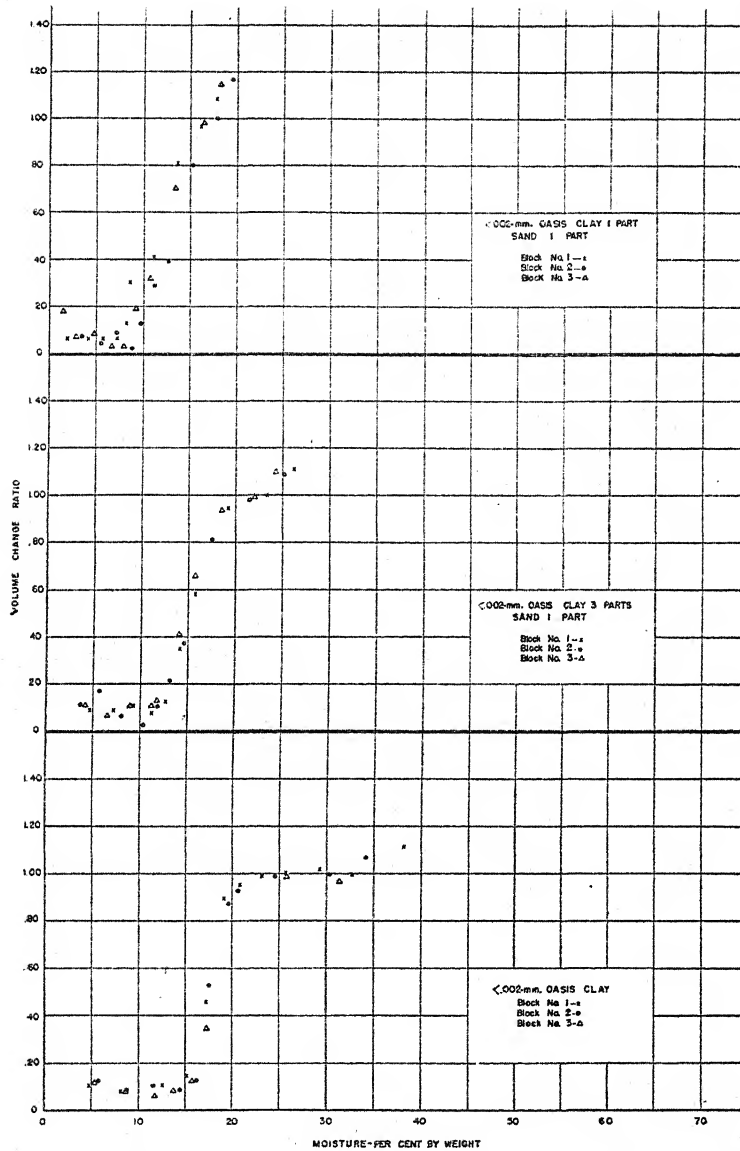


FIG. 8. VOLUME CHANGE RATIO FOR PLASTIC BLOCKS PREPARED OF THE <0.002-MM. CLAY FRACTION FROM OASIS SILT LOAM AND <0.002-MM. CLAY-SAND MIXTURES

cated in figures 7 to 12, in which are plotted the volume change ratios for blocks and clods. This tendency was greater with Oasis silt loam (figs. 8, 10, 11, and 12) than with Houston black clay (figs. 7, 9, 11, and 12).

The general trends of the volume change ratio for blocks and clods corresponding to the <0.002-mm. clay-sand mixtures are plotted in figure 11. These trend



curves are based on the points plotted in figures 7 to 10. The curves show that the shrinkage range is narrowed by the addition of sand in all cases for both

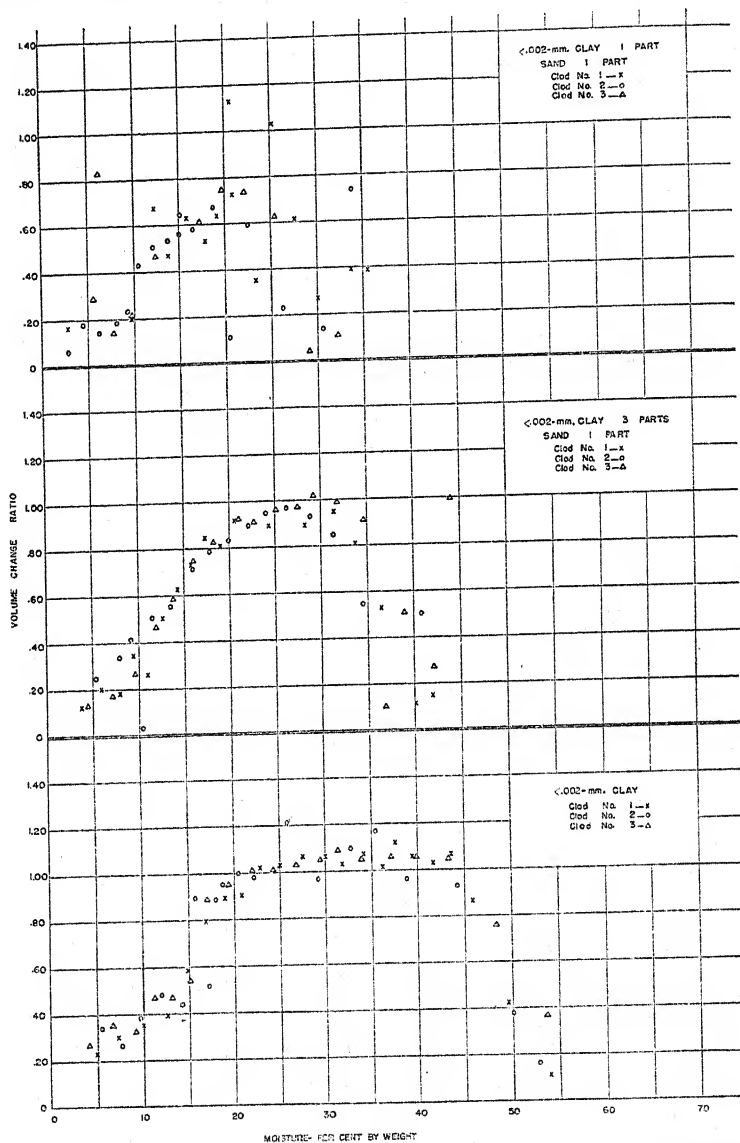


FIG. 9. VOLUME CHANGE RATIO FOR CLODS COMPOSED OF THE <0.002-MM. CLAY FRACTION OF HOUSTON BLACK CLAY AND <0.002-MM. CLAY-SAND MIXTURES

blocks and clods. Sand also caused the residual shrinkage to begin at a lower moisture content in the Oasis blocks and clods, but did not seem to influence the moisture content at which residual shrinkage occurred in Houston black clay in

either blocks or clods. At least the influence was not in the same order as the sand content. Increased sand reduced the maximum values of the volume

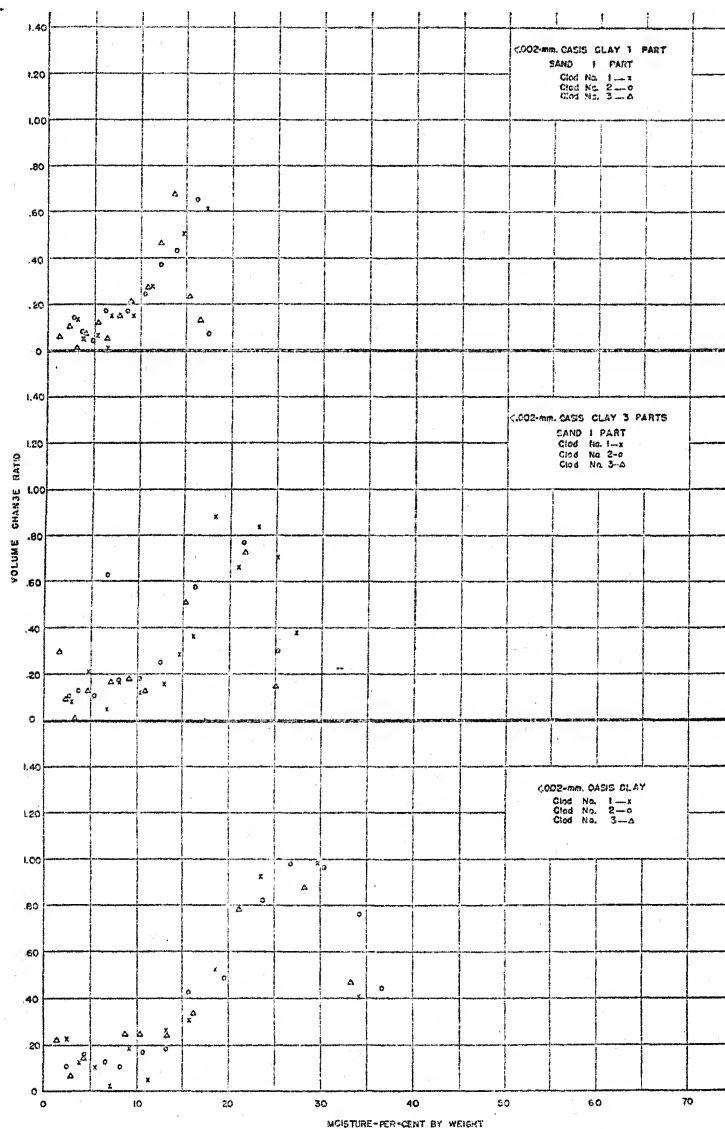


FIG. 10. VOLUME CHANGE RATIO FOR CLODS COMPOSED OF THE <0.002-MM. CLAY FRACTION OF OASIS SILT LOAM AND <0.002-MM. CLAY-SAND MIXTURES

change ratio for clods of both soils and caused the maximum to be attained at a lower moisture content. Since the volume change ratio is less than unity throughout the moisture range in the clods, with the lone exception of clods com-

posed of  $<0.002$ -mm. Houston black clay, it is evident some of the water lost as the soil dries is replaced by air through the moisture range over which shrink-

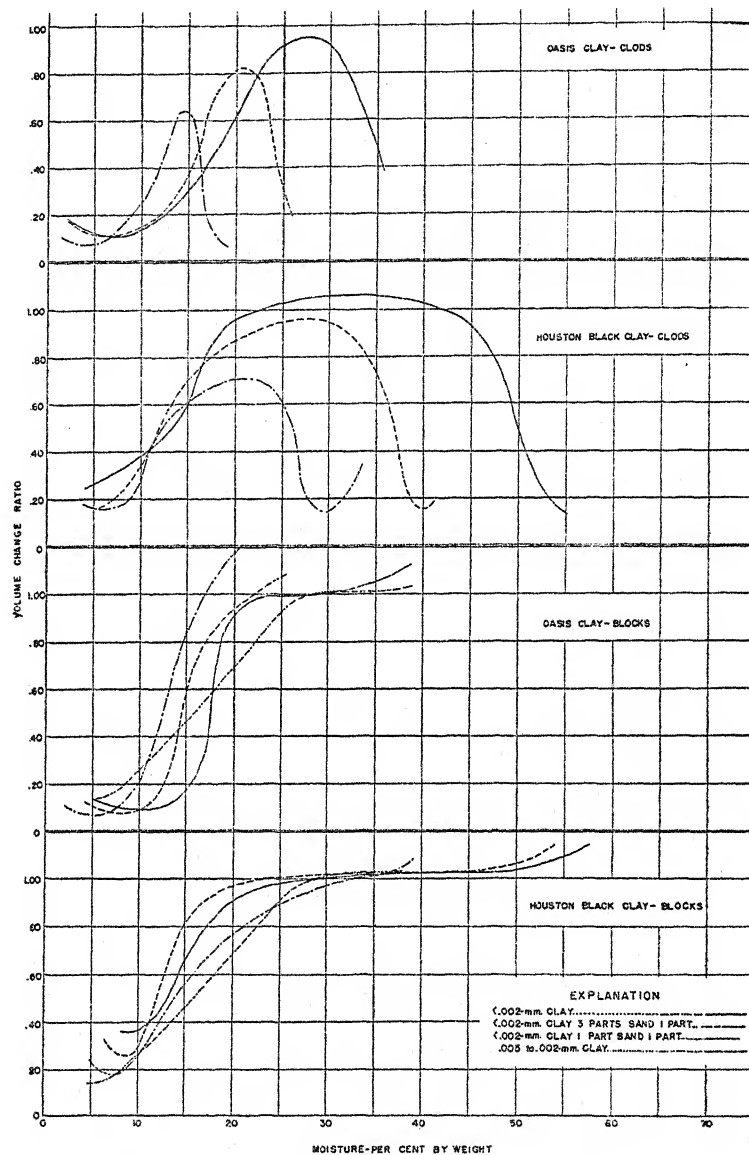


FIG. 11. TREND OF VOLUME CHANGE RATIO FOR PLASTIC BLOCKS AND CLODS REPRESENTING CLAY AND CLAY-SAND MIXTURES

age takes place. The amount and the rate of shrinkage that accompany drying of the materials studied are summarized numerically in table 4.

Organic matter in the form of alfalfa meal, as shown in figure 12, caused residual shrinkage to begin at a higher moisture content in Houston black clay blocks

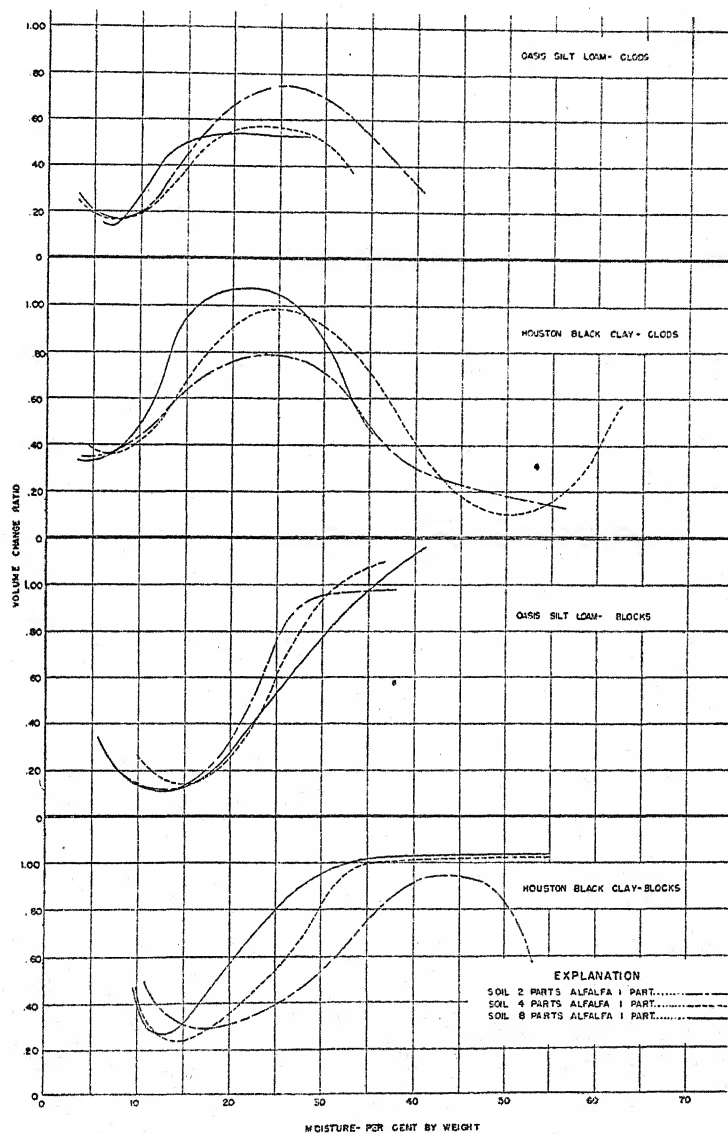


FIG. 12. TREND OF VOLUME CHANGE RATIO FOR PLASTIC BLOCKS AND CLODS REPRESENTING SOIL-ORGANIC MATTER MIXTURES

and at a lower moisture content in Oasis silt loam blocks. It eliminated normal shrinkage, for the most part, in Oasis silt loam and in the high organic matter mixture of Houston black clay. It is interesting to note that the shape of the

TABLE 4

*Shrinkage, specific volume, and moisture relationships of blocks and clods of Houston black clay and Oasis silt loam and of their sand and organic mixtures*

	SHRINKAGE		SPECIFIC VOLUME				
	Moisture range		Wet†	Dry‡	Change	Per cent change	Change per per cent moisture change
	Total shrinkage	Normal shrinkage*					
Blocks							
H.B.C.§ <0.002 mm. ....	58-7	58-10	.99	.52	.47	91	.0092
H.B.C. <0.002 mm. 3 pts., sand 1 pt.	53-5	53-10	.93	.50	.43	86	.0090
H.B.C. <0.002 mm. 1 pt., sand 1 pt.	40-4	40-20	.79	.52	.27	52	.0075
O.S.L.¶ <0.002 mm. ....	35-5	35-15	.73	.54	.19	35	.0063
O.S.L. <0.002 mm. 3 pts., sand 1 pt...	26-2	26-13	.66	.52	.14	27	.0058
O.S.L. <0.002 mm. 1 pt., sand 1 pt..	18-1	18-12	.58	.49	.09	18	.0053
H.B.C. 0.005-0.002 mm.....	38-4	38-22	.77	.53	.24	45	.0071
H.B.C. 0.005-0.002 mm. 3 pts., sand 1 pt.....	32-3	32-20	.72	.51	.21	41	.0072
H.B.C. 0.005-0.002 mm. 1 pt., sand 1 pt.....	25-2	25-14	.63	.51	.12	24	.0052
O.S.L. 0.005-0.002 mm.....	28-2	28-25	.67	.58	.09	16	.0035
O.S.L. 0.005-0.002 mm. 3 pts., sand 1 pt.....	23-1	23-19	.64	.54	.10	18	.0045
O.S.L. 0.005-0.002 mm. 1 pt., sand 1 pt.....	17-1	17-16	.56	.52	.04	8	.0025
H.B.C. 2 pts., alfalfa 1 pt.....	57-8	57-35	.90	.63	.27	43	.0055
H.B.C. 4 pts., alfalfa 1 pt.....	59-7	59-30	.94	.57	.37	65	.0071
H.B.C. 8 pts., alfalfa 1 pt.....	57-9	57-25	.94	.55	.39	71	.0081
O.S.L. 2 pts., alfalfa 1 pt.....	40-4	40-25	.76	.58	.18	31	.0050
O.S.L. 4 pts., alfalfa 1 pt.....	38-4	38-25	.76	.57	.19	33	.0056
O.S.L. 8 pts., alfalfa 1 pt.....	45-5	45-27	.83	.62	.21	34	.0053
Clods							
H.B.C. <0.002 mm. ....	56-2	43-19	1.03	.62	.41	62	.0076
H.B.C. <0.002 mm. 3 pts., sand 1 pt...	44-2	29-16	.91	.66	.25	38	.0060
H.B.C. <0.002 mm. 1 pt., sand 1 pt...	36-2	0	.83	.70	.13	19	.0038
O.S.L. <0.002 mm. ....	36-2	26-19	.84	.66	.18	27	.0053
O.S.L. <0.002 mm. 3 pts., sand 1 pt...	29-1	0	.75	.62	.17	27	.0061
O.S.L. <0.002 mm. 1 pt., sand 1 pt...	18-1	0	.66	.60	.06	10	.0035
H.B.C. 2 pts., alfalfa 1 pt.....	63-1	0	1.10	.83	.27	33	.0044
H.B.C. 4 pts., alfalfa 1 pt.....	65-3	0	1.10	.75	.35	47	.0056
H.B.C. 8 pts., alfalfa 1 pt.....	44-3	25-15	.99	.72	.27	38	.0066



TABLE 4—Continued

	SHRINKAGE		SPECIFIC VOLUME				
	Moisture range		Wet†	Dry‡	Change	Per cent change	Change per per cent moisture change
	Total shrinkage	Normal shrinkage*					
<i>Code—Continued</i>							
O.S.L. 2 pts., alfalfa 1 pt.....	41-2	0	.98	.78	.20	26	.0051
O.S.L. 4 pts., alfalfa 1 pt.....	34-2	0	.87	.72	.15	21	.0047
O.S.L. 8 pts., alfalfa 1 pt.....	29-5	0	.84	.69	.15	22	.0063

\* Volume change ratio approximately unity.

† Approximate sticky point.

‡ Oven-dry.

§ H.B.C. = Houston black clay.

|| O.S.L. = Oasis silt loam.

curve for the high organic matter mixture of Houston black clay resembles that of clods. The influence of organic matter on the volume change ratio representing clods of corresponding mixtures, as with blocks, was, in the main, reversed for the two soils. Increased organic matter resulted in a lower maximum value for the volume change ratio for Houston black clay and in a higher value for Oasis silt loam. In both soils organic matter displaced the maximum ratio in the direction of increased moisture content.

It is significant that without exception the apparent specific volume of plastic blocks is less than that of the corresponding clods (table 5). This suggests that a comparison between the dry specific volume of clods and of plastic blocks representing the same materials may be a measure of the porosity which exists in the soil mass by virtue of structural development or those conditions responsible for the presence of porosity greater than that which would exist under conditions of minimum apparent specific volume. The relationship is conveniently expressed as a ratio in which the apparent specific volume of the block is the divisor and the apparent specific volume of the clod the numerator. All ratios then would be greater than unity. The data indicate little correlation between the sand and organic matter content and the ratio.

#### DISCUSSION OF RESULTS

The character of the shrinkage curve appears to be related to the apparent specific volume of the soil mass and presumably the character of the pore space, particularly in the high moisture range. This confirms results previously published (5). In this connection, it would seem that aeration should not be a problem in soils in which so-called normal shrinkage is absent. Particularly where plastic blocks of the material fail to exhibit normal shrinkage, puddling should be less damaging, if indeed a possibility. The entrance of air in the wet range found to be associated with clods and absent in blocks points to the possi-

TABLE 5

*Relationship between the dry specific volume of clods and plastic blocks of the same material*

MATERIAL	CLODS			BLOCKS			RATIO*
	Specific volume	H <sub>2</sub> O	Pore space	Specific volume	H <sub>2</sub> O	Pore space	
		per cent	per cent		per cent	per cent	
Houston black clay 0.002 mm.	.625	4.1	39.7	.527	7.8	28.5	
	.617	4.3	38.9	.526	7.9	28.3	
	.625	3.2	39.6				
Average . . . . .	.622	3.8	39.4	.527	7.8	28.4	1.182
Houston black clay 0.002 mm. 3 parts, sand 1 part	.673	2.9	43.9				
	.641	4.4	41.1	.500	5.4	24.5	
	.663	3.2	43.1	.506	6.2	25.5	
Average . . . . .	.659	3.5	42.7	.503	5.8	25.0	1.309
Houston black clay 0.002 mm. 1 part, sand 1 part	.695	1.9	45.7	.531	4.3	28.9	
	.699	2.0	46.0	.560	6.3	32.6	
	.699	1.7	46.0	.541	4.9	30.2	
Average . . . . .	.698	1.8	45.9	.544	5.1	30.6	1.282
Oasis silt loam 0.002 mm.	.643	1.6	41.3	.539	3.6	29.9	
	.659	1.8	42.8	.543	4.0	30.5	
	.634	.5	40.5	.542	4.2	30.3	
Average . . . . .	.645	1.3	41.5	.541	3.9	30.2	1.193
Oasis silt loam 0.002 mm. 3 parts, sand 1 part	.645	2.3	41.5	.528	3.2	28.6	
	.602	1.5	37.3	.527	3.2	28.4	
	.610	1.8	38.1	.518	3.0	27.1	
Average . . . . .	.619	1.9	39.0	.524	3.1	28.0	1.181
Oasis silt loam 0.002 mm. 1 part, sand 1 part	.624	2.7	39.5	.495	.5	23.8	
	.623	2.2	39.4	.512	2.2	26.3	
	.609	.5	38.0	.500	1.1	24.5	
Average . . . . .	.618	1.8	39.0	.503	1.2	24.9	1.230
Houston black clay 4 parts, alfalfa 1 part	.710	2.02	46.9	.576	7.6	34.5	
	.756	.73	50.1	.587	11.0	35.7	
	.755	7.20	50.0	.594	12.6	36.5	
Average . . . . .	.740	3.32	49.0	.586	10.4	35.6	1.263
Houston black clay 8 parts, alfalfa 1 part	.742	4.28	49.2	.548	10.0	31.1	
	.707	2.89	46.7	.567	14.1	33.6	
	.718	.96	47.4	.558	9.7	32.3	

TABLE 5—Continued

MATERIAL	CLODS			BLOCKS			RATIO*
	Specific volume	H <sub>2</sub> O	Pore space	Specific volume	H <sub>2</sub> O	Pore space	
		per cent	per cent		per cent	per cent	
Average.....	.722	2.71	47.8	.558	11.3	32.3	1.294
Oasis silt loam 2 parts, alfalfa 1 part	.800	.13	52.8	.580	6.9	36.2	
	.768	1.19	50.9	.567	5.4	33.4	
	.787	1.09	52.0	.570	4.8	33.9	
Average.....	.785	.80	51.9	.572	5.7	34.5	1.372
Oasis silt loam 4 parts, alfalfa 1 part	.720	1.23	47.6	.577	4.3	34.5	
	.723	1.33	47.9	.567	6.4	35.4	
	.742	6.62	49.2	.586	9.2	35.7	
Average.....	.728	3.06	48.2	.577	6.6	35.2	1.262
Oasis silt loam 8 parts, alfalfa 1 part	.703	3.65	46.3	.610	5.5	37.3	
	.699	3.91	46.0	.619	5.3	39.0	
	.676	4.22	44.2	.613	6.3	38.4	
Average.....	.693	3.93	45.5	.614	5.7	38.2	1.129
Salt Lake silt loam†	.561	1.69	32.7	.512	2.1	26.3	
	.550	1.67	31.4	.516	2.8	26.9	
	.557	1.68	31.9				
	.555	2.15	31.9				
	.549	2.13	31.8				
	.567	2.33	33.4				
Average.....	.556	1.96	32.1	.514	2.4	26.6	1.081

$$\text{* Ratio} = \frac{\text{Dry specific volume (clod)}}{\text{Dry specific volume (block)}}$$

† Series name will probably be changed when soil is correlated.

bility that lack of aeration is a factor in the depressed plant growth associated with puddled soils and, conversely, that soil structure promotes better growth through better aeration. This is not a new concept, but the data perhaps adds some enlightenment to the subject. It should be observed, however, that some pore space was occupied by air at the time shrinkage measurements were begun on all blocks and clods (table 6). The percentage of pore space occupied by air initially increased with increasing sand content. There is some evidence that the percentage of air in the soil mass may be a factor influencing the character of shrinkage. The data presented, however, are not adequate to warrant any conclusions on this point. The percentage of air in plastic blocks can be modified, to some small degree at least, by the method of preparation.

Part of the absorbed ions on the clay from Oasis silt loam is doubtless  $\text{Na}^+$  whereas that on the Houston black clay is  $\text{Ca}^{++}$ . This may, in part, account for the difference in the shrinkage observed for the two soils, since Hofmann and

TABLE 6  
*Distribution of air and water in pore space when shrinkage measurements on blocks and clods began*

	CLODS			BLOCKS		
	Pore space	H <sub>2</sub> O	Air	Pore space	H <sub>2</sub> O	Air
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
Houston black clay	62.85	56.36	6.49	61.90	58.36	3.54
	62.26	53.16	9.10	61.04	56.98	4.06
	63.81	56.83	6.98			
Average. ....	62.97	55.45	7.52	61.47	57.67	3.80
Houston black clay 1 part, sand 2 parts	58.64	43.37	15.27			
	56.09	40.92	15.17	59.81	54.14	5.67
	58.74	44.11	14.63	59.36	52.81	6.55
Average. ....	57.82	42.80	15.02	59.59	53.48	6.11
Houston black clay 1 part, sand 1 part	54.78	36.01	18.77	51.46	38.33	13.13
	54.26	34.50	19.76	53.20	40.80	12.40
	54.19	33.13	21.06	52.33	39.38	12.95
Average. ....	54.41	34.55	19.86	52.33	39.50	12.83
Oasis silt loam	53.90	35.72	18.18	48.12	35.00	13.12
	55.04	37.06	17.98	48.72	35.63	13.09
	53.09	34.73	18.36	47.27	34.42	12.85
Average. ....	54.01	35.84	18.17	48.04	35.02	13.02
Oasis silt loam 1 part, sand 2 parts	49.64	28.99	20.65	42.54	27.15	15.39
	46.58	26.70	19.88	42.23	26.81	15.42
	46.69	25.72	20.97	40.73	25.65	15.08
Average. ....	47.64	27.14	20.50	41.83	26.54	15.30
Oasis silt loam 1 part, sand 2 parts	43.53	17.84	25.69	34.11	18.56	15.55
	42.91	17.78	25.13	35.89	19.87	16.02
	42.17	16.82	25.35	34.52	18.80	15.72
Average. ....	42.87	17.48	25.39	34.84	19.08	15.76

Bilke have shown that the lattice spacing associated with the absorption of water is less for  $\text{Na}^+$ -saturated montmorillonite than for  $\text{Ca}^{++}$ - and  $\text{H}^+$ -montmorillonites. An explanation for the influence which sand had on the dry appar-

ent specific volume cannot be offered. It is difficult to understand why in Oasis silt loam the dry apparent specific volume decreased as the sand content increased for both blocks and clods and why, in Houston black clay, sand did not influence the dry apparent specific volume of the blocks but increased that of the clods. There seems to be no reason to question the data, but, because of the need for an explanation, it is desirable that the tests be repeated, and if the differences are substantiated a search be made for the basis of this difference in behavior of the two soils. Nothing is known concerning the mineral composition of the clay components of these soils. Oasis clay, however, is dispersed more readily than is Houston black clay, and because of this it is possible that Oasis clay arranges itself as a coating on the sand grains whereas Houston black clay tends to occupy the space between the grains as separate or independent particles. Since the real specific gravity is the same as that of sand, the clay fraction of Houston black clay might be expected to occupy approximately the same volume as an equal weight of sand where structural porosity is lacking, as exemplified by plastic blocks, and more space in the clods, where some structural porosity is present. Alfalfa meal, as has been pointed out, influenced the character of shrinkage in the two soils quite differently (fig. 12). Just what significance these differences imply as regards the composition, use, and management of the two soils is not fully understood.

Attention might be directed to individual determinations, wherein the volume change ratio departs markedly from the general trend. These departures at first were the cause of concern for the accuracy of the measurement, but it is believed now that these departures are normal occurrences and the result of adjustments in the soil mass as the material dries. In support of this explanation, the data indicate that the frequency and degree of deviation between successive measurements are greater for the more porous, less stable materials such as clods and organic matter mixtures than for normal soil. Moreover, shrinkage and swelling measurements<sup>7</sup> employing a collodion coating, as described by Sideri (8), resulted in highly erratic values for the volume change ratio. The only explanation that can be offered for the greater variation in volume change ratio observed for clods coated with collodion compared to those coated with paraffin is the possibility that the collodion casing imparts a stress on the soil mass, thereby inducing more frequent and greater volume adjustments within the mass.

The most significant contribution of this investigation is believed to be the possibility which the data suggest for a quantitative measurement of the structural status of soils. The size distribution of the pore space in soil as measured by Leamer and Shaw (6) and others, aggregate analysis, and total porosity determinations have all been used as an index of soil structure. None of these, however, measures the structural level in terms of the degree to which structural development has progressed or deteriorated. A comparison of the dry apparent specific volume of clods and plastic blocks of the same material is believed to offer such a measure.

<sup>7</sup> Data on shrinkage and swelling obtained by this method have not been included in this presentation.



Whether or not the kneading employed in the preparation of plastic blocks produces a packing arrangement of the individual soil particles such that the mass occupies the minimum volume when dry is not indicated by the data. It is evident, however, as previously shown (table 5), that the apparent specific volume of dry plastic blocks is smaller than that of corresponding clods, and that the dry apparent specific volumes of the blocks prepared from the same material vary little one from another. Irrespective, then, of the degree of compaction of the material in the blocks, it would appear that the dry apparent specific volume of plastic blocks provides a reference which is characteristic of the material and that a comparison of porosity in the plastic block and in the clod is a measure of the relative porosity resulting from structural development. The amount the apparent specific volume of the clod exceeds that of the block, or the higher the ratio (table 5), the greater the relative porosity and, presumably, the better the structural condition of the soil. Considerable variation has been found to exist between clods representing the same sample of soil. This should be expected because of the heterogeneous nature of soil.

It will be observed that the moisture content for which the dry apparent specific volume is reported is not constant. This is a source of error, since the apparent specific volume decreases with drying. The fact that the values are not fully comparable is recognized but is not considered serious, since in this low moisture range the apparent specific volume changes but little with further reduction of moisture. To overcome this objection, greater care could be exercised to ensure reduction of the moisture content to the same level at the time the final determinations are made. Data on the apparent specific volume of soils representing field conditions, recognized as examples of different degrees of structural development or levels of deterioration, are not available at present. Obviously a study which would provide these data is necessary before the merit of the approach can be fully judged.

#### SUMMARY

Results of shrinkage measurements on a number of soils and clay-sand and soil-alfalfa meal mixtures are reported. The effect of sand on shrinkage varied with the soil or clay component of the mixture. In general, however, it was found to narrow the range more than to alter the character of the shrinkage until the sand content reached 25 to 50 per cent. Organic matter in the form of alfalfa meal had little effect on the shrinkage range but modified the character of the shrinkage and the apparent specific volume. Sand and organic matter influenced the apparent specific volume differently, depending on the clay or soil with which it was incorporated.

It was found that the dry apparent specific volume of clods was invariably higher than that of plastic blocks prepared from the same material. Based on this relationship, it is suggested that a comparison of the dry apparent specific volume of clods and blocks affords a measure of the pore space which exists in the soil by virtue of structural development.

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# DETERMINATION OF SOIL ORGANIC MATTER BY MEANS OF A PHOTOELECTRIC COLORIMETER<sup>1</sup>

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Determination of soil organic matter by the wet combustion method of Schollenberger,<sup>2</sup> has been subjected to many modifications. Most of these modified methods are suitable for soil research laboratories, but they require trained personnel and are time-consuming. Use of an inside indicator with its titration to the proper end point has been found difficult by untrained personnel. A simple, fool-proof, yet accurate method seems desirable, therefore, for routine soil-testing laboratories. The percentage of organic matter in the soil is a valuable help in making recommendations to the farmer for applications of lime and nitrogen. Consequently the following investigation was undertaken in the hope that the method could be made more efficient for simple laboratory routine by means of a photoelectric colorimeter.

## ESTABLISHING THE METHOD

Reports of a detailed investigation of the problem of determining soil organic matter by wet combustion were recently published by Walkley.<sup>3</sup> His summary covers most of the factors on digestion, except that he did not stress uniformity in the method used for mixing concentrated sulfuric acid with potassium dichromate. The conditions of digestion considered to be important by Walkley were acid strength, size of reacting vessel, and air temperature. In the present investigation, these factors were tested separately, and each was found to be important. The method of mixing concentrated sulfuric acid with the soil and with the potassium chromate solution also proved to be important. Strict detailed attention must be paid to each.

Modification of the method to allow use of a photoelectric colorimeter seemed reasonable, since the color of normal potassium dichromate is orange, which changes to green while oxidizing the organic matter. This color change was found to be proportional to the amount of organic matter in the sample.

In order to establish the method, several samples of soil containing organic matter ranging from 0.5 to 5.5 per cent, as determined by complete oxidation in a combustion train,<sup>4</sup> were carried through the wet combustion process, diluted

<sup>1</sup> Contribution from the Department of Soils, Missouri Agricultural Experiment Station, Journal Series No. 1058.

<sup>2</sup> Schollenberger, C. J. A rapid method for determining soil organic matter. *Soil Sci.* 24: 65-68. 1927.

<sup>3</sup> Walkley, A. A critical examination of a rapid method for determining organic carbon in soils—effect of variations in digestion conditions of inorganic soil constituents. *Soil Sci.* 63: 251-264. 1947.

<sup>4</sup> Winters, E. Jr., and Smith, R. S. Determination of total carbon in soils. *Indus. and Engin. Chem. (Analyt. Ed.)* 1: 202-204. 1929.

with water, and allowed to settle. The supernatant liquids were then transferred to adsorption tubes, and readings, to be used as indexes, were taken on the photoelectric colorimeter. The greatest spread in readings from low organic matter content to high was obtained by using one plate of red and one plate of yellow

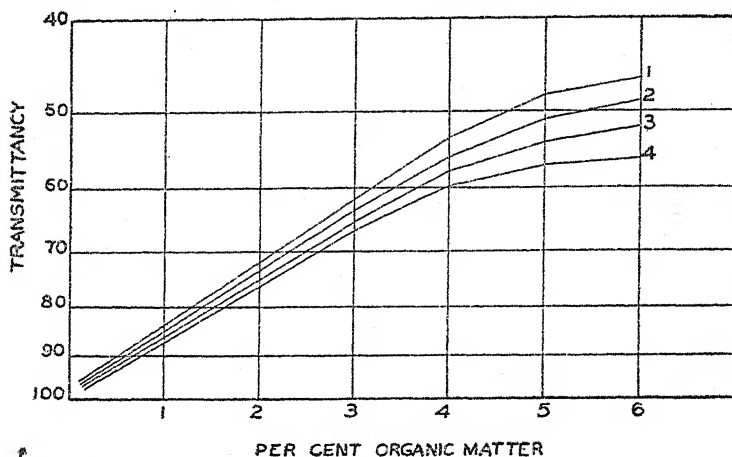


FIG. 1. TRANSMITTANCY CURVES FOR SOIL ORGANIC MATTER UNDER EXTREMELY VARIABLE CONDITIONS OF DIGESTION

Transmittancy obtained with a red 645  $m\mu$  filter cell 1.5 cm. diameter; conditions of digestion: curve 1—room temperature 30°C., sulfuric acid 96 per cent; curve 2—room temperature 20°C., sulfuric acid 96 per cent; curve 3—room temperature 20°C., sulfuric acid 94 per cent; curve 4—room temperature 15°C., sulfuric acid 94 per cent.

TABLE 1

*Comparison of organic matter contents of soils as determined by the rapid method and by total combustion*

SAMPLE NUMBER	ORGANIC MATTER, COMBUSTION METHOD	RAPID METHOD—TECHNICIAN A		RAPID METHOD—TECHNICIAN B	
		Transmittancy*	Organic matter	Transmittancy*	Organic matter
	<i>per cent</i>		<i>per cent</i>		<i>per cent</i>
1	0.92	88.0	0.80	87.0	0.89
2	1.25	83.5	1.15	82.0	1.28
3	2.41	70.0	2.38	69.5	2.40
4	3.53	59.0	3.60	58.5	3.65
5	5.20	51.5	4.95	50.5	5.15

\* The standard soil used contained 2.30 per cent organic matter and gave a transmittancy of 70.5. Therefore curve 2 was used for this set of determinations.

filter glass. A spread great enough for practical use can be obtained by using red filters near 620  $m\mu$ . The instrument used in this investigation was a Cenco "Photometer" equipped with a red (645  $m\mu$ ) filter.

The results of these investigations indicated that a given curve, established



for one set of conditions, could not be used over a long period. The conditions of digestion and procedure may vary from time to time, as may individual differences. Changes in the concentration of sulfuric acid and room temperature were most common. Therefore, a family of curves was prepared (fig. 1) under variable conditions, including all the extremes encountered. Then, by carrying a standard soil sample (the percentage of organic matter of which should be determined by use of the combustion train) through the standard procedure along with a batch of unknown soils, the correct curve for that set of analyses can be determined and used for the unknown samples.

The method has proved to be (a) extremely accurate for soils containing less than  $2\frac{1}{2}$  per cent organic matter, (b) less accurate for those soils in the range of  $2\frac{1}{2}$  to  $4\frac{1}{2}$  per cent, and (c) still less accurate for those above  $4\frac{1}{2}$  per cent.

#### METHOD

The method as finally developed is as follows: Weigh or measure 1 gm. of 10-mesh air-dry soil into a 250-ml. Erlenmeyer flask. Add 10 ml. of normal potassium dichromate. By means of a 250-ml. glass stopcock burette, add rapidly 20 ml. of concentrated sulfuric acid. Quickly swirl the mixture for 10 seconds and allow it to stand for 10 minutes. Then add 100 ml. of water. This mixture should stand for 4 or 5 hours<sup>5</sup> to allow time for the supernatant liquid to become clear. Pour the supernatant liquid into adsorption tubes and read on the photoelectric colorimeter. By selecting the proper curve for standard soils, the percentage of organic matter in the unknowns can be determined.

It is convenient to set up 25 to 40 samples at a given time, then readings can be made later.

#### EXPERIMENTAL RESULTS

A comparison was made of the percentages of organic matter in several widely different soils as determined by total combustion and by the rapid method. The rapid method determinations were made by two different technicians. The results are given in table 1.

#### SUMMARY

A simplified method of determining soil organic matter is described. Measurement of the color of the supernatant liquid in the oxidizing mixture by means of an electric colorimeter was found to be speedy and accurate when calibrated against a standard known soil. This eliminates the extra step of titration in the process, and simplifies the routine sufficiently for almost any careful manipulator.

<sup>5</sup> Should a longer time interval be desirable, the curve to be used must be checked by carrying a standard soil for the same time interval.



# KAOLIN AND TREATED KAOLINS AND THEIR REACTIONS<sup>1</sup>

ALFRED T. PERKINS

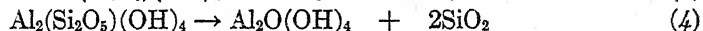
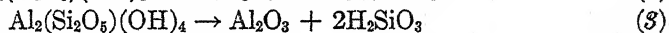
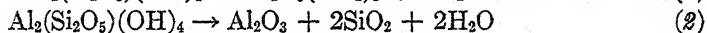
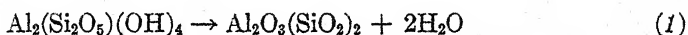
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Kaolin, an important soil mineral, has been widely studied by soil chemists. Not only is kaolin of great importance in soils, but it is widely used in commerce and industry. The base-exchange capacity of kaolin and its reactions with anions and other characteristics have been widely studied. Thermal curves of the mineral have been obtained and its atomic structure has been determined by means of x-rays and other methods. The chemical composition of the mineral has been determined, electron microscope studies have been made, and other data have been collected. In many cases kaolin has been ground or otherwise treated and the residual material studied as kaolin. That a mineral such as kaolin could be finely ground and retain its original characteristics has been widely accepted.

The purpose of this paper is to report certain changes in activity and characteristics of kaolin during grinding or heating, some of which are characteristic of other minerals. The data reported also indicate a method of approach in studying the formation of soil clay minerals.

Studies of the chemical composition and possible decomposition of kaolin and the atomic ratios of the various component elements indicate the following interesting possibilities:



As kaolin disintegrates, not only might the above compounds be obtained but also many other silicic acids, aluminum oxides or hydroxides, and combinations of these elements. Commonly recognized aluminum oxides and hydroxides are  $\text{Al}_2\text{O}_3$ , alumina;  $\text{AlOOH}$ , diaspore;  $\text{Al}_2\text{O}(\text{OH})_4$ , bauxite;  $\text{Al}(\text{OH})_3$ , gibbsite.

Some commonly recognized silicic acids and minerals corresponding to these polymerized silicates are  $\text{H}_2\text{SiO}_3$ , monometasilicic acid, pyroxenes;  $\text{H}_2\text{Si}_2\text{O}_5$ , dimesosilicic acid, clays;  $\text{H}_4\text{Si}_4\text{O}_{10}$ , tetraparasilicic acid, talc;  $\text{H}_8\text{Si}_8\text{O}_{11}$ , tetramesosilicic acid, amphibols.

<sup>1</sup> Paper presented at a meeting of the American Chemical Society, Kansas City, June, 1947. Contribution No. 329, of the Department of Chemistry, Kansas Agricultural Experiment Station. Since the preparation of this paper, a publication along the same line by Laws and Page (Laws, W. D., and Page, J. B. changes produced in kaolinite by dry grinding. *Soil Sci.* 62: 319-336. 1946.) has appeared. The present paper checks in part the data presented by those investigators and adds to these data.

## PREPARATION OF SAMPLES

Kaolin obtained from Langly, South Carolina, was ground to pass through a 100-mesh sieve, thoroughly mixed, and subdivided into four portions. Portion A was retained in its original condition. Portion B was heated overnight in an electric muffle at 700°. This treatment resulted in a loss in weight of nearly 14 per cent, which is the theoretical loss according to the equation (1) or (2). Portion C was ball-milled in a porcelain jar with porcelain pebbles for 10 days. The ball mill was frequently stopped to uncake the material. There was little change in weight of this sample during grinding. Portion D was ground in a mullite mortar with a mullite pestle operated by a mechanical grinding device. Five-gram portions of kaolin were ground for 48 hours. This period of grinding was selected because it was found to be the minimum required to remove the thermal dip in kaolin as shown in figure 1. This material is subsequently referred to as "mortar-ground kaolin."

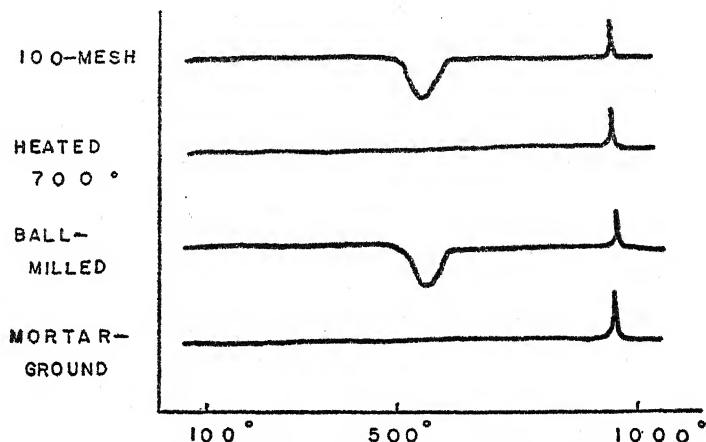


FIG. 1. THERMAL CURVES OF KAOLIN AND TREATED KAOLINS

## METHODS

The four samples of kaolin or prepared kaolin were analyzed for  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  by A.O.A.C. methods (1). The  $\text{Al}_2\text{O}_3$  was precipitated by ammonium hydroxide as for  $\text{R}_2\text{O}_3$ . Mechanical analysis was made by dispersing the kaolin in a dilute ammonium hydroxide solution, with the aid of a Waring Blendor, and separating the particles by sedimentation, evaporating the suspension to dryness, and weighting the residue. Calculation of sedimentation time was based on Stokes' law, and sedimentation was accelerated by the use of a centrifuge. Base-exchange capacity was determined by leaching the sample with neutral normal ammonium chloride solution until equilibrium was obtained, followed by the removal of excess electrolyte by 80 per cent alcohol. The ammonium ion was released from the mineral by magnesium oxide and quantitatively determined by Kjeldahl distillation. Phosphate fixation was

determined by the method outlined by Perkins and King (10). Essentially, the procedure consisted of the addition of water,  $H_3PO_4$  and HCl or NaOH to the mineral, shaking overnight at  $25^\circ$ , and determining the phosphate in the supernatant liquid by the coeruleomolybdate method of Atkins (2). The pH values of the mineral suspensions were determined with a glass electrode. The thermal curves were determined by the method outlined by Grim (4).

#### DISCUSSION OF RESULTS

From the data presented, it is quite clear that the several treatments of kaolin radically alter this mineral. Such an alteration is indicated in the literature. Insley and Ewell (6) have shown that heating kaolin will result in an alteration of the mineral in accord with equation (2). Jackson and Truog (7) found that fine grinding of minerals, including kaolin, will increase their water solubility. This is supported by the data on particle size given in table 2, which indicates an alteration in the mineral. Stout (13) and Ravikovitch (12), among others, suggested that phosphate fixation by minerals is a function of the replacement of OH ions by phosphate ions. Hendricks (5) showed that base exchange is principally on the lateral faces of kaolin minerals; and Johnson and Lawrence (9), among others, found that in kaolinite base-exchange capacity is a direct function of specific surface.

The data presented in this paper show that heating the kaolin does not affect its base-exchange capacity but does increase phosphate fixation. Grinding kaolin increases base-exchange capacity and also phosphate fixation. Both grinding and heating kaolin increase the alkalinity of the mineral except at high pH values, where the acidity of the ground samples is increased. Thus it is seen that grinding kaolin produces a mineral that not only is more active in combining with anions but also is amphoteric.

The data in table 1 indicate that heating decomposes the kaolin with the elimination of water, but that there is no other change in its ultimate chemical composition. No change in chemical composition appears to be effected by grinding.

The mechanical analyses of the samples (table 2) show that when kaolin is ground in a mortar, about 11 per cent of its weight is lost during water suspension and subsequent evaporation to dryness on the hot plate. This loss is probably due to an alteration of the kaolin mineral according to equations somewhat similar to (1), (2), (3), and (4). According to Mellor (9), aluminum trihydrate loses its water at  $310^\circ$  and aluminum dihydrate at  $540^\circ$ , whereas if equation (1) or (2) were induced by grinding, the water could be driven off at much lower temperatures. As the thermal curves give no indication of loss of water for the mortar-ground kaolin, it is assumed that grinding induces equation (1) or (2). Since the ground kaolin yields a smaller amount of Al and Si, the indications are that it has adsorbed water; this is to be expected, as the material is palpably very finely ground. The differences in weight losses between the ball-milled and mortar-ground samples indicate a difference in degree of grinding. It is recognized that the finely ground aluminum oxides and silica might be highly active, and it is probable that the freshly ground  $Al_2O_3$  and  $SiO_2$  when placed in a water



suspension would react to form gels which would aggregate to form larger particles. On this account the data in table 2 should be recognized as mechanical analyses after water suspension, and not as an actual analysis of the material in the dry state. Additional support for the aggregation of the fine particles is given by Perkins and King (10), who were unable to separate kaolin particles of approximately 50 to 100  $\mu$  diameter.

The base-exchange capacity determinations in milliequivalents per 100 gm. were as follows: 100-mesh kaolin, 2.0; heated to 700°, 2.0; ball-milled, 16.0; mortar-ground, 12.6. These data agree with reports of Johnson and Lawrence (8) and others. The fact that heating will not increase base-exchange capacity even though grinding will, and that the two grinding treatments theoretically

TABLE 1  
*Chemical composition of kaolin and treated kaolins*

KAOLIN SAMPLE	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> MOLECULAR RATIO
	<i>per cent</i>	<i>per cent</i>	
Theoretical.....	46.50	39.50	1.95
100-mesh.....	46.37	39.49	1.95
Heated 700°.....	53.02	45.48	1.95
Ball-milled.....	44.37	37.40	1.95
Mortar-ground.....	44.32	37.38	1.95

TABLE 2  
*Mechanical analysis of kaolin and treated kaolins*  
Percentages of particles in various size groups

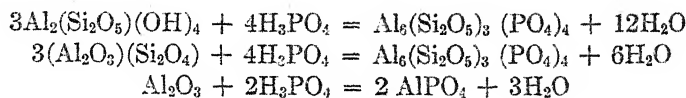
KAOLIN SAMPLE	0.0002 MM.	0.0002-0.00063 MM.	0.00063-0.00200 MM.	0.002 MM.	TOTAL
100-mesh.....	12.05	25.00	26.57	36.38	100.00
Heated 700°.....	0.00	16.15	30.22	54.86	101.23
Ball-milled.....	9.54	13.70	19.32	56.30	98.86
Mortar-ground.....	15.72	22.12	29.95	23.97	91.76

induce the same decomposition aside from particle size show the effect of surface area on this phenomenon.

Table 3 shows that any treatment that removes the OH groups from the kaolin increases phosphate fixation. It is rather hard to evaluate the factor of particle size and the energy factor involved in removing the OH groups. Perkins (10) has shown in comparing pyrophyllite  $[\text{Si}_4\text{O}_{10}\text{Al}_2(\text{OH})_2]$  with talc  $[\text{Si}_4\text{O}_{10}\text{Mg}_3(\text{OH})_2]$ , and muscovite  $[\text{KAlSi}_3\text{O}_{10}\text{Al}_2(\text{OH})_2]$  with phlogophite  $[\text{KAlSi}_3\text{O}_{10}\text{Mg}_3(\text{OH})_2]$ , that phosphate fixation is a function of the metallic ion to which the OH group is attached. The phosphate fixation curves for these aluminum and magnesium minerals agree with the aluminum and magnesium phosphate solubility curves of Gaarder (2).

The phosphate fixation equations suggested by Stout (13) and others, though

theoretical, may be accepted. Several theoretical equations of kaolin, dehydrated kaolin, and kaolin decomposition products with phosphoric acid are as follows:



It would be reasonable to assume that any reaction that would remove the OH radical or weaken the OH bonds would increase phosphate fixation.

The thermal curves in figure 1 indicate that the ball-milled kaolin had not been ground sufficiently to break the kaolin structure but that the mortar-ground kaolin had been disintegrated to the point where the water was freed. It seems probable that the water was driven off by the thermal treatment at a temperature too low to be recorded by the curve. As the water had already been removed from the heated kaolin, the thermal curve shows no exothermic reaction at 580°.

TABLE 3  
*Phosphate fixation by kaolin and treated kaolins*

KAOLIN SAMPLE	PERCENTAGE ADDED PHOSPHATE FIXED*														
	pH 2.0	pH 2.5	pH 3.0	pH 3.5	pH 4.0	pH 4.5	pH 5.0	pH 5.5	pH 6.0	pH 6.5	pH 7.0	pH 7.5	pH 8.0	pH 8.5	pH 9.0
100-mesh.....	6.0	21.0	30.0	38.0	38.0	39.0	35.5	32.0	30.0	24.0	26.0	24.0	13.0	2.0	X
Heated 700°..	0.0	24.0	60.0	85.0	97.0	96.0	88.0	74.0	63.0	39.0	24.0	22.0	15.0	6.0	3.0
Ball-milled...	30.0	52.0	68.0	100.0	100.0	100.0	100.0	100.0	100.0	98.0	92.0	68.0	73.0	41.0	26.0
Mortar-ground.....	5.0	25.0	52.0	94.0	97.0	100.0	100.0	100.0	100.0	99.0	95.0	78.0	60.0	48.0	37.0

\* Reaction adjusted with HCl or NaOH: 5 gm. kaolin + 0.01777 gm.  $\text{H}_3\text{PO}_4$  + HCl or NaOH, + approximately 25 ml.  $\text{H}_2\text{O}$ .

The data in table 4 show that heating kaolin increases its alkalinity and that grinding not only increases its alkalinity in the acid range of pH values but produces an amphoteric material. The amount of hydrochloric acid required to adjust the pH value of the mortar-ground kaolin to a pH value of 2.0 is more than 100 times that required to adjust a similar amount of the 100-mesh kaolin. The corresponding amount of base required to reach a pH value of 9.0 is about four times as great. It is therefore evident that as kaolin disintegrates in the soil it will have a considerable effect on the reaction of the soil at any point below neutrality. The values in table 4 must be weighted, in view of the fact that not only was kaolin present but also a small amount of  $\text{H}_3\text{PO}_4$ , and therefore the indicated acidity is greater than that of the kaolin alone. As kaolin disintegrates, the pH value of the soil suspension should tend to become more alkaline.

The miscellaneous data in table 5 support the other data presented. The "activity" of the kaolin is an indication of the reaction between the kaolin and the glass of a pyrex beaker. These data were noted during evaporation of the

samples in mechanical analysis and are a rough measure of the affinity between the mineral and the glass. In the mortar-ground kaolin, the attraction may be very great, especially near the surface of the liquid. An actual etching of the beaker occurred, making it necessary to discard the first set of analyses and repeat the evaporation under different conditions. This definitely indicates a disintegration or activation of the mineral. The data on puddling correlate with the activity, reaction, phosphate fixation, and base-exchange data. Grinding kaolin definitely alters the mineral so that its characteristics are greatly changed. Equation (2) probably results from grinding kaolin.

TABLE 4

*Reaction of kaolin and treated kaolins with acids and bases*

Milligram equivalents of hydrochloric acid or sodium hydroxide required to adjust 100 gm. of kaolin + 0.36 gm.  $H_2PO_4$  to indicated pH value

KAOLIN SAMPLE	pH 2.0	pH 2.5	pH 3.0	pH 3.5	pH 4.0	pH 4.5	pH 5.0	pH 5.5	pH 6.0	pH 6.5	pH 7.0	pH 7.5	pH 8.0	pH 8.5	pH 9.0
100-mesh.....	10.0	3.2	0.8	1.2	2.0	2.8	3.2	3.6	4.4	5.2	6.4	7.2	8.0	9.2	10.4
Heated 700°..	100.0	75.2	34.0	9.2	0.8	0.4	0.4	0.8	2.0	3.2	4.8	6.0	7.6	8.8	10.4
Ball-milled...	376.0	344.0	308.0	100.0	4.8	1.6	0.8	0.0	0.8	2.4	3.6	6.8	12.4	21.2	30.0
Mortar-ground.....	1360.0	1032.0	636.0	100.0	5.2	1.2	0.4	0.0	0.4	2.4	5.2	10.0	20.0	30.0	42.4

TABLE 5

*Miscellaneous properties of kaolin and treated kaolins*

KAOLIN SAMPLE	ACTIVITY*	COLOR†	PUDDLING‡
100-mesh.....	low	white	little
Heated 700°.....	medium	whiter	little
Ball-milled.....	high	white with gray tinge	little
Mortar-ground.....	very high	white with gray tinge	much

\* Action between the mineral and pyrex glass beakers when the mineral in water suspension was being evaporated during mechanical analysis.

† Color of the mineral especially when wet with water or alcohol.

‡ Caking on the filter during washing out of electrolyte in base-exchange determinations.

## SUMMARY

Phosphate fixation by kaolin, heated kaolin, and ground kaolin has been investigated as well as certain other reactions and characteristics of the minerals. Heating or grinding definitely alters the mineral, so that the reactions and characteristics of the residual mineral are greatly altered. Heating the kaolin eliminated about 13 per cent of its weight as water, increased particle size, did not change its base-exchange capacity, increased phosphate fixation, increased the alkalinity of the mineral, and made it somewhat whiter in color. Grinding the kaolin markedly increased its base-exchange capacity, increased its phosphate-fixing capacity, increased its alkalinity, and darkened its color somewhat. The

chief differences between the effects of heating and grinding are the changes in base-exchange capacity and phosphate fixation. This is interpreted to mean that base exchange is a function of surface area, whereas phosphate fixation is a function of the OH radicals as well as of surface area. Grinding kaolin probably results in the equation:



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## AZOTOBACTER INOCULATION OF CROPS: III. RECOVERY OF AZOTOBACTER FROM THE RHIZOSPHERE

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Almost from the time that *Azotobacter* was first described by Beijerinck as a microorganism capable of fixing free nitrogen, statements have been made that this bacterium is closely associated with cultivated plants and that it may be inoculated advantageously on the roots thereof. Allison (1) has reviewed this literature, particularly the Russian, and the several claims that many crops respond profitably to *Azotobacter* inoculation.

Knowledge concerning the extent to which *Azotobacter* may be established upon roots, and more broadly, how this organism responds to influences of the rhizosphere, is limited. Hiltner (7) believed that free-nitrogen-fixing bacteria were stimulated by root growth. Starkey (14) cited scattered references that *Azotobacter* is especially favored by cruciferous plants. Poschenreider (11) examined the roots of crucifers and found *Azotobacter* present; he then extended his work and found this bacterium associated with the roots of a wide variety of plants (12). His observations have been cited in support of the contention that *Azotobacter* is particularly adapted to the rhizosphere. Careful reading of Poschenreider's papers, however, shows that he used enrichment cultures only, and therefore his results can hardly be considered as quantitative. In fact, at certain seasons of the year he could not find *Azotobacter* in the closer rhizosphere, even though the organism was present in the adjacent soil. Truffaut and Vladymkov (15) reported *Azotobacter* generally present in the rhizosphere of wheat, but again, the criticism may be made that their observations were qualitative, as they did little more than record the presence of some rapidly growing and easily recognized soil organisms. Several of the microbes they named in addition to *Azotobacter* can hardly be considered as rhizophilic organisms. Neither Clark (3) nor Jensen (8) found *Azotobacter* in the rhizosphere of wheat growing in soils generally free of *Azotobacter*. Krassilnikov (10) reported that *Azotobacter* was depressed by the roots of plants. Recently, Katznelson (9) failed to note any positive rhizosphere response to mangels by *Azotobacter*, even though other microbial groups were markedly stimulated.

Allison *et. al.* (2) have failed to duplicate the Russian successes with *Azotobacter*. From some of their data, they concluded that there is no indication that *Azotobacter* can live in the rhizosphere and supply appreciable benefit to the growing plant. This conclusion was based primarily on yield data. Without

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bacteriological studies, there remains some question concerning the extent to which *Azotobacter* can be established on plant roots by inoculation. The work reported here was undertaken to obtain quantitative information on the occurrence of *Azotobacter* on plant roots following its addition thereto by means of mass culture applications, and to determine its response to the rhizosphere of growing plants.

#### EXPERIMENTAL

In the first of the experiments here reported, Webster loam of pH 5.9 was employed. In this soil lot no *Azotobacter* could be demonstrated initially by soil plaque or enrichment culture methods.

Forty glazed pots were filled with 800-gm. portions of soil. Single tomato seedlings (Pan-Americana) grown in a flat of the same soil, were transplanted when 17 days old. Ten plants were established without seedling treatment. In a second series, 10 pots were established with seedlings the roots of which had been dipped into a turbid suspension of *Azotobacter vinelandii*. This suspension, containing 95 million viable *A. vinelandii* per milliliter, was prepared from the surface growth on mannitol-agar. Another series of 10 pots was established with seedlings the roots of which had been dipped into a turbid suspension of *A. chroococcum*, containing 40 million viable cells per milliliter. The fourth series of 10 pots was established with seedlings the roots of which had been dipped into a heavy suspension (1 part of Azotogen to 2 parts of water) of Russian-prepared Azotogen<sup>2</sup>. The Azotogen as received contained a total microbial population of 340 million microorganisms per gram and 15 million *A. chroococcum* per gram.

At the time of transplanting, each seedling root dipped into *Azotobacter* suspension also received 5 ml. of the same suspension pipetted on and around the seedling root as it was being set into soil.

One pot was removed from each series on the fourth and eighteenth day after transplanting, and two pots were removed on the twenty-seventh, forty-ninth, sixty-seventh, and seventy-fifth days. All root samples collected were studied culturally for *Azotobacter* content, as were also the soil samples collected on the fourth, forty-ninth, sixty-seventh, and seventy-fifth days. Initial and final samples (at 4 and at 75 days) from each series were studied for total microbial number and for denitrifying and nitrifying populations as well.

*Azotobacter* was determined by spotting on mineral-salts mannitol-agar plates a total of 20 aliquots, each 1/100 ml., from each of three or more successive serial dilutions. After 4 days' incubation at 30° C., each point of inoculation was read as either positive or negative for *Azotobacter*. If there was any doubt as to the correct reading, Gram-staining was employed. The most probable number of *Azotobacter* present per gram of sample material studied was determined from tables for quantitative bacteriology (6).

*Azotobacter* populations determined for 40 root samples are shown in table 1. It may be noted that there was a consistent decline in *Azotobacter* numbers from

<sup>2</sup> Azotogen supplied by F. E. Allison, from a lot prepared by scientists of the All-Union Institute of Agricultural Microbiology, USSR.

the initially high levels established by inoculation. It may also be noted that uninoculated root samples of tomato plants grown in an Azotobacter-free soil yielded no Azotobacter.

Inoculation with Azotobacter was found to have no effect on total microbial number, or on numbers of nitrifying or denitrifying bacteria. Azotobacter populations determined for soil samples collected from pots at time of removal of roots are shown in table 2.

In a second greenhouse experiment, the persistence of Azotobacter on tomato seedlings heavily inoculated at time of transplanting to a soil normally containing Azotobacter was determined. This experiment was similar in all respects to

TABLE 1

*Numbers of Azotobacter determined at varying intervals following inoculation of tomato roots grown in Azotobacter-free soil*

DAYS FOLLOWING INOCULATION	NUMBERS OF AZOTOBACTERS*			
	Seedlings inoculated with			Uninoculated
	<i>A. vinelandii</i>	<i>A. chroococcum</i>	Azotogen	
4	7,420†	1,589‡	1,970‡	0
18	2,750	869	379	0
27	2,750	4,280	792	0
	2,750	1,250	622	0
49	428	1,620	170	0
	171	2,400	109	0
67	150	40	49	0
	101	28	62	0
75	28	79	49	0
	74	38	62	0

\* In thousands per gram of gross root material.

† This column represents *A. vinelandii* population.

‡ These columns represent *A. chroococcum* population.

the previous one except that the soil lot employed was Webster loam of pH 6.2, which, after screening and mixing, showed one thousand Azotobacter per gram. Tomato seedlings, from the flat previously described, were transplanted when 21 days old. Aliquots of the Azotobacter suspensions prepared for the first series of inoculations were stored for 4 days at 4° C. until used in this work. The inoculation treatments employed were the same as those previously described for Azotobacter-free soil. Eleven pots per treatment, or 44 pots in all, were established.

For microbiological studies, one pot was removed from each series on the fourteenth day after transplanting of seedlings, and two pots were removed on

TABLE 2

*Numbers of Azotobacter determined for soil, initially free of Azotobacter, at varying intervals following transplanting of heavily inoculated tomato seedlings*

DAYS FOLLOWING TRANSPLANTING	NUMBERS OF AZOTOBACTER*			
	Seedlings inoculated with			Uninoculated
	<i>A. vinelandii</i>	<i>A. chroococcum</i>	Azotogen	
4	493†	589‡	231‡	0
49	278	230	49	0
	174	230	62	0
67	230	33	28	0
	162	79	27	0
75	43	35	10	0
	55	70	6	0

\* In thousands per gram of soil.

† This column represents *A. vinelandii* population.

‡ These columns represent *A. chroococcum* population.

TABLE 3

*Numbers of Azotobacter determined at varying intervals following inoculation of tomato roots grown in soil normally containing Azotobacter*

DAYS FOLLOWING INOCULATION	NUMBERS OF AZOTOBACTER*			
	Seedlings inoculated with			Uninoculated
	<i>A. vinelandii</i>	<i>A. chroococcum</i>	Azotogen	
14	7,920	3,490	493	<0.2
24	2,750	2,750	391	7.3
	2,400	3,490	329	8.6
36	2,280	1,710	10	10.0
	2,400	493	15	10
55	920	1,200	12	2.0
	1,200	540	7	2.0
65	79	62	10	1.0
	12	116	3	1.0
72	29	24	16	1.7
	33	62	49	2.8

\* In thousands per gram of gross root material.

the twenty-fourth, thirty-sixth, fifty-fifth, sixty-fifth, and seventy-second days. Azotobacter populations determined for the root and soil samples collected are presented in tables 3 and 4.

It was again found that inoculation with *Azotobacter* had no effect on total microbial number or on numbers of denitrifying or nitrifying bacteria.

Observations were made on the incidence and survival of *Azotobacter* in uncropped soil maintained moist in the greenhouse.

Webster loam of pH 5.9 maintained fallow for 3 months showed no *Azotobacter* at any biweekly sampling.

TABLE 4

*Numbers of Azotobacter determined for soil, normally containing Azotobacter, at varying intervals following transplanting of heavily inoculated tomato seedlings*

DAYS FOLLOWING TRANSPLANTING	NUMBERS OF AZOTOBACTER*			
	Seedlings inoculated with			Uninoculated
	<i>A. vinelandii</i>	<i>A. chroococcum</i>	Azotogen	
14	329	550	120	1.0
24	101	116	62	.8
	49	225	40	1.9
36	62	542	3.9	26.3
	70	101	4.9	4.9
55	54	54	3.3	1.5
	162	162	1.3	1.2
65	160	35	4.0	1.3
	...	...	...	1.3
72	12	54	1.5	.7
	43	54	1.5	1.0

\* In thousands per gram of soil.

Webster loam of pH 6.2, when maintained fallow and at 60 per cent of moisture-holding capacity, showed the following numbers of *Azotobacter* per gram:

Initial level.....	1,000
After 2 weeks.....	4,930
After 4 weeks.....	6,000
After 6 weeks.....	2,230
After 8 weeks.....	3,290
After 10 weeks.....	1,190
After 12 weeks.....	2,290

These populations are comparable to those encountered in this soil lot cropped, uninoculated, to tomatoes (cf. table 4).

A study was made of the survival of *Azotobacter* in certain aliquots of Webster loam of pH 5.9 after establishment of such bacteria therein by mass inoculation. Those aliquots of soil from which tomato seedlings had been removed 4 days after inoculation were repotted and then maintained fallow. *Azotobacter*



numbers were determined for soil portions removed on the forty-fifth, sixty-third, and seventy-ninth days following inoculations. Likewise, the survival of Azotobacter was studied in Webster loam of pH 6.2 from which heavily inoculated tomato plants were removed after 24 days of growth. Results are shown in table 5. More viable Azotobacter were maintained in the uncropped than in the cropped soil portions.

TABLE 5  
*Survival of Azotobacter added to uncropped soil*

DAYS AFTER INOCULATION	INOCULUM USED	AZOTOBACTER* IN UNCROPPED SOIL	EXCESS*† OVER CROPPED PORTION
<i>Webster loam pH 5.9, initially Azotobacter-free</i>			
45	<i>A. vinelandii</i>	230	4
	<i>A. chroococcum</i>	240	10
	Azotogen	70	56
63	<i>A. vinelandii</i>	230	34
	<i>A. chroococcum</i>	240	204
	Azotogen	43	28
79	<i>A. vinelandii</i>	230	182
	<i>A. chroococcum</i>	106	53
	Azotogen	13	8
<i>Webster loam pH 6.2, Azotobacter normally present</i>			
45	<i>A. vinelandii</i>	93	27
	<i>A. chroococcum</i>	141	0
	Azotogen	14	9
65	<i>A. vinelandii</i>	201	41
	<i>A. chroococcum</i>	63	28
	Azotogen	7	3
85	<i>A. vinelandii</i>	87	60
	<i>A. chroococcum</i>	175	121
	Azotogen	12	11

\* In thousands per gram of soil.

† For same or closest comparable date of sampling.

The better survival of Azotobacter in soil portions from which tomato plants had been removed than in the corresponding portions cropped to tomatoes suggested the possibility that root fragments left in soil after removal of plants might stimulate Azotobacter, even though the living roots showed no such effect. This possibility was investigated by removing four tomato plants (each grown for 30 days after being transplanted, without inoculation, in Webster loam pH 6.2) and collecting, manually and by soil sieving, as much of the total root material present as practicable. Each potted soil lot was divided into two half-portions, and the

recovered root material was mixed into one half-portion. The portions were repotted and maintained at 60 per cent of moisture-holding capacity for 1 month. Azotobacter was determined at weekly intervals. Observations are given in table 6.

In order to determine the rhizosphere response of Azotobacter to some plants other than the tomato, Webster loam of pH 6.2 was cropped to mustard, broccoli, and soybeans under greenhouse conditions. This soil lot contained Azotobacter, and no inoculations were employed. Increase in numbers of Azotobacter was not occasioned by the growth of any of these plants. It will suffice to summarize the data obtained for soil cropped to mustard.

Mustard plants were grown in each of four glazed pots. Duplicate soil samples removed at 3 weeks showed 4,930 and 6,000 Azotobacter per gram, and at 5

TABLE 6  
*Comparison of Azotobacter populations in soil portions with and without added tomato root fragments*

REPLICATES	NUMBERS OF AZOTOBACTER* AFTER VARIOUS INTERVALS OF INCUBATION				
	None	1 week	2 weeks	3 weeks	4 weeks
<i>Half-portions with root fragments removed</i>					
A-	730	1,930	920	2,750	4,900
B-	1,010	2,310	780	2,750	1,200
C-	1,470	2,310	6,300	3,290	2,750
D-	1,470	3,290	3,990	2,750	3,290
<i>Half-portions with root fragments present</i>					
A+	450	1,470	600	3,290	2,310
B+	1,010	3,290	1,470	2,750	2,750
C+	1,220	11,600	4,930	2,550	1,470
D+	1,690	2,750	3,290	2,550	2,750

\* Per gram of soil.

weeks, 2,230 and 3,290. All plants were removed at 7 weeks; soil and root samples were collected from all pots. Numbers of Azotobacter for the replicate soil samples were 3,880, 5,890, 2,750, and 1,640. These populations are no greater than those encountered in portions of this soil maintained fallow. Numbers of Azotobacter per gram of freshly collected mustard roots at 7 weeks were as follows for the replicate samples: 3,290, 2,750, 2,750, and 11,600.

Cropping to broccoli for 6 weeks or to soybeans for 11 weeks likewise failed to increase the Azotobacter content of this soil.

#### DISCUSSION

In the current work, unusually high numbers of Azotobacter were established in soil by the addition of bacterial suspensions. In the 2 to 3 months following additions, Azotobacter populations steadily decreased. Fedorov and Tepper (4)

have noted a sharp drop in the number of *Azotobacter* on the roots of millet following inoculation.

The observation that *Azotobacter* persisted as well in slightly acid soil initially containing no *Azotobacter* as in a more neutral soil, together with the steadily decreasing numbers in both soils, suggests that no continued multiplication of the inoculated species occurred. However, as the numbers observed within the first 30 days after inoculation were higher than could be accounted for simply from addition of known suspensions, and as both cropped and fallow soil lots of pH 6.2, uninoculated, showed increases over their initial levels within the first 30 days following establishment, the possibility of some multiplication of *Azotobacter* after inoculation must be admitted. Such a response, if it does occur, must be temporary. Greaves (5) asserted that a few organisms placed in a new environment already containing millions can seldom hope to gain ascendancy over the organisms naturally present and struggling for countless generations to adapt themselves to the environment.

The more rapid disappearance of added *Azotobacter* from cropped than from uncropped soil may be due to any one of a number of factors, or to combinations of them. The increased concentrations of microorganisms occurring on roots (3, 14) may result in microbial interactions or antagonisms adversely affecting *Azotobacter*. Competition for and removal of nutrients by plant roots, or differences in aeration and other environmental conditions established in the cropped soils likewise may have been instrumental in hastening the disappearance of added *Azotobacter*.

The adverse effect of cropping was noted only against the high populations of *Azotobacter* established by bacterial additions. Within the normal range of *Azotobacter* numbers, roots of soybeans, tomatoes, broccoli, and mustard were found to have neither an adverse nor a noticeably stimulatory effect on *Azotobacter*. Apparently, *Azotobacter* is one bacterium little affected by the presence of plant roots, in contrast to the distinctly positive rhizosphere responses of certain other bacteria, for example, *Radiobacter* (13).

Waksman and Starkey (16) reported that it is quite likely that soil becomes enriched in nitrogen because of nonsymbiotic development of nitrogen-fixing bacteria about plant roots. They pointed out that this might be possible because (a) in the neighborhood of growing roots of plants there is an excretion of soluble carbohydrates and addition of other residues to the soil which may serve as food for the bacteria and because (b) plants rapidly consume most of the available combined nitrogen from this part of the soil, and hence, rapid development of *Azotobacter* and *Clostridium* would be favored.

Present knowledge would indicate that rapid development of *Azotobacter* in the sense of increased numbers is not occasioned by growing roots. It is possible that the presence of an available supply of energy material and a nitrogen minimum might enable *Azotobacter* to fix nitrogen efficiently and in significant amounts where otherwise it would not do so. In the preceding paper of this series, Allison *et al.* (2) obtained no evidence of nitrogen fixation or of increased yield by *Azotobacter* inoculation. In the work here reported, no evidence has

been accumulated to show that *Azotobacter* responds favorably to the presence of plant roots.

## SUMMARY

Suspensions of *A. chroococcum* and *A. vinelandii* were applied to tomato seedlings at time of transplanting to (a) soil initially free of *Azotobacter* and (b) soil normally containing *Azotobacter*. Root and soil samples were collected for microbiological studies at numerous intervals within the range of 4 to 75 days after transplanting.

In both soils, there was a rapid decline from the initially high numbers of *Azotobacter* established by inoculation procedures.

The disappearance of added *Azotobacter* was found to be less rapid in uncropped than in cropped soil.

Inoculation with *A. chroococcum*, *A. vinelandii*, and Azotogen did not alter the microflora of tomato roots, insofar as revealed by studies of total microbial number and numbers of nitrifying and denitrifying bacteria.

Addition of tomato root fragments to soil did not affect the *Azotobacter* content of Webster loam normally carrying *Azotobacter*.

The *Azotobacter* flora of soil normally containing these bacteria was no greater when such soil was cropped to tomatoes, to soybeans, to broccoli, or to mustard than when it was maintained fallow.

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## BOOKS

*Annual Review of Microbiology*. Volume 1. Edited by CHARLES E. CLIFTON. Annual Reviews, Inc., Stanford, California, 1947. Pp. 404.

This is the first volume of a series that is expected to follow much the same pattern as that of the Annual Reviews of Biochemistry. It contains up-to-date articles on protozoa, malarial parasites, phytopathogenic fungi and viruses, bacterial metabolism, nitrogen metabolism, industrial fermentations, quaternary ammonium compounds, antibiotics, chemotherapeutic agents, immunochemistry, enteric infection, the rickettsiae, and respiratory viruses. A list of references is appended to each article, the number averaging more than 100. The reviews are critical appraisals of the literature and, as such, should save much time and energy for others in the same field. Judged by the quality of material in the first volume, this series is destined to become a highly important part of the literature in this field.

*Basic Botany*. By FRED W. EMERSON. The Blakiston Company, Philadelphia, 1947. Pp. 372, profusely illustrated. Price \$4.

This book is written for beginning students in botany. The subject matter is fitted around the protoplasmic unit. The physiology, anatomy, morphology, taxonomy, genetics, and ecology of plants are considered, not as separate subjects but wherever they fit into the picture. The first third of the book deals with life, leaves, food, energy, nutrients, water, roots, and stems. The remainder of the book deals with the evolutionary aspects of plant life and the characteristics of the several classes of plants. Finally, consideration is given to plant associations and successions and to checks and balances that operate in their control. The material is well organized and presented. The illustrations are excellent.

*Calcium and Phosphorus in Foods and Nutrition*. By HENRY C. SHERMAN. Columbia University Press, New York, 1947. Pp. 179, figs. 7. Price \$2.75.

This is a concise presentation of a more detailed book which the author hopes to publish in due time. It deals with the special importance of calcium and phosphorus in the nutrition of animals and man. The most significant point developed is that the diet of herbivorous animals tends to be deficient in phosphorus because such animals consume large amounts of the vegetative portion of plants. In contrast, the diet of man tends to be deficient in calcium because humans generally consume more of the seed portions of plants. The importance of greenleaf vegetables and milk as sources of calcium is emphasized. The members of the Chenopodiaceae are excepted from the recommended vegetables because of their high content of oxalic acid, which renders the calcium unavailable. A selected bibliography of some 500 references is appended. The book provides interesting and important reading.

*Chemical Insect Attractants and Repellents.* By VINCENT J. DETHIER. The Blakiston Company, Philadelphia, 1947. Pp. 289, figs. 69. Price \$5.

The purpose of this book is to present a theoretical basis for the study of insect attractants and repellents in an attempt to replace the cut-and-try procedures that have long been employed. The 10 chapters include consideration of the nature of chemical attractants, essential oils and related substances, fermentation products, protein and fat decomposition products, olfactometers and threshold concentrations, baits and traps, repellents, chemical basis of taste and olfaction, and evolution of feeding preferences. Reference is made to some 1500 papers that were reviewed in preparation for writing the book. The material is so presented as to make it highly interesting not only to the entomologist but to the lay reader as well. All those having to do with plant production will find this book of considerable value.

*Diseases of Field Crops.* By JAMES G. DICKSON. McGraw-Hill Book Company, Inc., New York, 1947. Pp. 429, figs. 102. Price \$4.50.

The purpose of this book is to present material necessary for a working knowledge of the diseases affecting farm crops. It has been evolved over a period of 20 years of classroom instruction. The author offers it to the public free of royalties. The diseases covered are those affecting barley, corn, millet, oats, rice, rye, sorghums, sugar cane, wheat, grasses, alfalfa, clovers, soybeans, cotton, flax, and tobacco. Preceding the discussion of specific diseases is a chapter on the physiological anatomy of plant groups in relation to disease. The appendix includes a list of crop diseases arranged in relation to the causal factor and another of the orders and families of bacteria and fungi that are parasitic on crop plants. Each chapter ends with a set of references, which sometimes attain a total of more than 250. The illustrations are excellent, as is also the method of presentation of the material. The book merits a place on the reference shelves of all those who deal with problems of crop production.

*The Evolution of Gossypium.* By J. B. HUTCHINSON, R. A. SILOW, AND S. G. STEPHENS. Oxford University Press, New York, 1947. Pp. 160, figs. 10, plates 11. Price \$4.50.

This book gives the results of 20 years of research into the origin of the cotton plant and its development as a crop. It is the final report of the genetics department, Cotton Research Station, Trinidad, B.W.I. It is divided into four parts: classification of the genus *Gossypium*, evolution of the species, differentiation of the true cottons, and significance of *Gossypium* in evolutionary studies. The unique feature about the research reported in the book is that it was designed to cover the entire genus, including all the wild species. The value of a knowledge of the wild species becomes apparent in connection with the development of new combinations and in the exploitation of variability in fitting cotton to climate and in choosing lint characters to meet the needs of industry. The authors point to the overemphasis placed on varieties of the American Cotton Belt, indicating that other upland stocks are available that offer additional possibilities. A list of about 150 references is appended.

*The Grassland of North America.* By JAMES C. MALIN. Printed by the author, 1541 University Drive, Lawrence, Kansas, 1947. Pp. 398. Lithoprinted, paper bound. Price \$3.

The author indicates that this book constitutes merely an introduction to the history of the grassland of North America. The book is divided into two parts, the first of which deals with sciences and regionalism and the second with historiography. In the first part, consideration is given to ecology, climatology, geology, edaphology, grass formations, early explorations, and factors in grassland equilibrium. The second part is largely concerned with the pioneering work of such men as Josiah Strong, N. S. Shaler, E. W. Hilgard, F. H. King, H. L. Shantz, and Isaiah Bowman. A bibliography of some 1500 references is appended. The book contains some highly interesting and informative material and should be of special interest to agricultural workers in the grassland area.

*Growth Regulators.* By JOHN W. MITCHELL AND PAUL C. MARTH. The University of Chicago Press, Chicago, 1947. Pp. 129, figs. 16. Price \$2.50.

As the foreword says, the newest thing in gardening and horticulture is the increasing use of plant hormones and growth-regulating chemicals. This book lists the common growth-regulating chemicals and their uses and then goes into detailed consideration of weed control; vegetative propagation; transplanting trees, shrubs, and herbaceous, climbing, and trailing plants; preventing growth in stored plant materials; preventing fruit drop; ripening fruit; improving fruit set; producing seedless fruit; and certain other plant responses to growth-regulating chemicals. A page of important producers of these chemicals is appended. The book will be of considerable value to all those who are concerned with this field of science as well as to those who are in position to apply the recommendations in gardening and horticultural practice.

*Nature and Prevention of Plant Diseases.* Second edition. By K. STARR CHESTER.

The Blakiston Company, Philadelphia, 1947. Pp. 525, figs. 224. Price \$5.

This book was written to meet the needs of students whose formal training in plant pathology is limited but who need to know something definite about practical means of controlling plant diseases. This involves an understanding of the nature and the requirements of disease organisms affecting crop plants. The several chapters deal with the practical significance of disease, types of disease, rusts, smuts, mycorrhizae, scabs, wilts, downy mildews, damping-off diseases, blights, viruses, dodder and similar parasites, nematodes, physiogenic diseases, identification of disease organisms, environmental factors affecting them, and the principles and procedures of control by regulation, developing resistance, and use of cultural methods. The book is exceptionally well illustrated and provides highly interesting reading.

*Principles of Micropaleontology.* By MARTIN F. GLAESSNER. John Wiley and Sons, Inc., New York, 1947. Pp. 296, plates 14, figs. 64. Price \$6.

As the name indicates, this book deals with the microorganisms of the past, their structure, biology, and genetic relationships, and their distribution in

time and space. The several parts have to do with the present status of this science, classification, collecting, and studying microfossils, paleontology of the Foraminifera, and stratigraphic micropaleontology. The most important application of this science is in connection with explorations for oil, but it is useful at times in drilling for water and in certain types of engineering projects. Since the findings of the petroleum industry, as a rule, are not published, it is only through such a book as this that newcomers to the field can get their start. The last chapter is devoted entirely to equipment employed in exploring for oil. The appendix contains a revised classification of the Foraminifera and a bibliography of some 700 pages.

*The Response of Crops and Soils to Fertilizers and Manures.* By W. B. ANDREWS. Published by the author, State College, Mississippi, 1947. Pp. 459, figs. 82. Price \$4.50.

This book is the product of 10 years of teaching a course on the response of crops to fertilizers and 17 years of experimentation in this field of study. The several chapters deal with crop response to nitrogen, use of anhydrous and aqua ammonia, use of Cyanamid, effect of fertilizers on availability of mineral nutrients, calculating effect of fertilizers on lime content of soils, use of legumes as green manures, effect of green manures on lime and potash content of soils, effect of removal of nitrogen and mineral elements in crops on yield of crops that follow, soil organic matter, importance of lime, response of crops to mineral fertilizers and sodium, production and use of nitrogen fertilizers, mixed fertilizers, buying fertilizers, effect of fertilizer placement on stand and yield, manure as an agent for return of nitrogen and mineral elements, fertilizing fish ponds, and effect of fertilizers on yield and feeding value of hay and pasture crops. A list of references is appended to each chapter. The chapter on the use of anhydrous ammonia and aqua ammonia, with its excellent illustrations, is of special interest. Those who have to do with teaching or research in the use of fertilizers will find the book of interest and value.

*The Scientists Speak.* Edited by WARREN WEAVER. Boni and Gaer, New York, 1947. Pp. 369. Price \$3.75.

This book contains 79 radio addresses that were sponsored by the United States Rubber Company in an attempt to develop a scientific program of general interest to the public. Each address was prepared and presented by a specialist in the field covered. The several addresses are arranged in chapters in accordance with their relationships to the others. These chapters cover the science of the earth, of the sky, of new materials and improved processes, of new instrumental techniques and new chemicals, of atoms and molecules, of physics and mathematics, of chemistry and living things, of plants and animals, of fundamental biology, of ourselves, of health, of nature and society, of war, and of long-term values. For specialists in soils and plants, the papers on plant roots, bacteria, fungi, hybrid corn, and world population are of special importance. Of greater interest to most scientists, however, are the popular presentations of

material in those fields of science with which they are less familiar. The book should have a wide appeal.

*A Second Look.* By EDWARD H. FAULKNER. University of Oklahoma Press, Norman, 1947. Pp. 193. Price \$3.

This book is designed to answer the many questions raised by readers of *Plowman's Folly*, the original contribution of this author, which has enjoyed very wide distribution. The emphasis seems to have been changed somewhat from the disadvantages of the moldboard plow to the advantages of the disc or similar implement for incorporating organic matter into the surface soil rather than plowing it under. Similarly, advocacy of omission of fertilizers as being unnecessary is now more largely confined to those carrying nitrogen. Faulkner's concepts are closely allied with those of Sir Albert Howard, Lady Eve Balfour, Louis Bromfield, and J. I. Rodale, all of whom believe that more soil organic matter and better use of it provide the remedy for most diseases affecting plants, animals, and man.

*Soil Science Society of America Proceedings, 1946.* Volume 11. The Soil Science Society of America, Morgantown, West Virginia, G. G. Pohlman, Secretary-Treasurer, 1947. Pp. 572. Price \$5.

This highly important volume of proceedings contains 3 general papers dealing with new discoveries in soil science and 100 special papers discussing specific pieces of research. These latter papers are grouped under physics, chemistry, microbiology, fertility, technology, and genesis, morphology, and cartography of soils. A symposium was held on "transmission of water through soils in relation to irrigation and pond construction" and two papers were presented before a forest-soils subsection. Every man who is concerned with soil science will find in this volume a number of papers of direct interest and many others that have corollary value. The volume is of special importance to graduate students who are majoring in soils, because of the wide variety of topics presented and the many excellent lists of literature that are cited.

*Soilless Growth of Plants.* Second edition. By TOM EASTWOOD. Reinhold Publishing Corporation, New York, 1947. Pp. 277, figs. 101. Price \$4.75.

This is a greatly improved and enlarged edition of the book of the same title originally written by Carleton Ellis and M. W. Swaney. The author's commercial experience with soilless culture of plants has resulted in the production of a book that answers most of the questions facing the beginner in this field. The chapter titles include general plant physiology, water culture, sand culture, gravel culture, the nutrient solution, technical control of the nutrient solution, technical control of the plant culture, common detriments, special chemicals, and analyses of the nutrient solution. A two-page list of selected references is appended. Anyone who wants to know the details about growing plants without soil will find this a very useful book.

THE EDITORS.





## INFLUENCE OF COMPOSITION OF PLANT MATERIALS ON PROPERTIES OF THE DECOMPOSED RESIDUES<sup>1</sup>

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The origin, composition, and properties of soil organic matter have long been subjects of much study and controversy. The term "humus," which has been highly abused in designating different organic substances, dates back to the time of the Romans, when it was frequently used to designate the soil as a whole (27). Wallerius (28), in 1761, was the first to define "humus" in terms of decomposed organic matter, but the prevailing ideas concerning the chemical nature of organic matter and the mechanism of its formation were still very vague.

Even in the early part of the present century many still believed that the "humic acids" originated from carbohydrates, regardless of whether they were natural compounds or preparations obtained by treatment of carbohydrates with acids (4, 8, 11, 27). Eller helped to clear up some of the confusion in 1925 when he found that on oxidation of phenols and their derivatives, products were obtained which were similar in their chemical and physical properties to the natural "humic acids" (5). According to him (6), the "humic acids" obtained by treatment of carbohydrates with mineral acids have nothing in common with the natural products, in spite of a superficial similarity. Waksman has said that one may feel justified in abandoning without reservation the whole nomenclature of humic acids with the possible exception, because of its historical importance, of the term "humus"; and that this term should be used to designate the organic matter of the soil as a whole (27).

The role of lignin in the formation of "humus" has been investigated by many workers, and though their conclusions have varied greatly, it is now accepted that lignin plays an important part in the formation of "humus" and in its chemical properties. Some of the conflicting views have been caused by the difficulties in estimating the exact amount of lignin present in decomposing plant materials.

Much effort has been spent in trying to maintain an adequate supply of organic matter in agricultural soils. Because organic matter is a constituent which should be maintained in the soil in relatively large amounts and at the same time one which must be continuously in process of decomposition, the maintenance of a good supply in cultivated soils will inevitably involve periodic additions.

In view of the fact that the nature and composition of soil organic matter depend on the nature of the parent material from which the organic matter is derived, and through their influences on the actual population, the conditions under which that material is decomposed, more advantageous additions might be made

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if more information were available on the amount of organic matter derived from different plants or the constituents thereof, and on the effect of this material on the properties of the soil. The purposes of this work were (a) to ascertain the effect of varying the proportions of certain major constituents of plant materials on the course of decomposition and (b) to determine the contribution made by individual plant constituents to the properties of the decomposed residues obtained therefrom and the effects of the residues on some properties of soil.

Oxidation studies were planned in the hope of developing a method that would facilitate the study of the nature of organic matter in soils and determine the quantities therein.

#### EXPERIMENTAL PROCEDURE

##### *Materials used*

Thurman loamy fine sand was chosen for this work because of its low organic matter content, about 1 per cent. In such a soil, the effects produced by the added organic materials should be most pronounced and probably most easily measured.

The organic materials added were untreated oat straw; oat straw preparations with varying proportions of lignin, cellulose, and hemicellulose; dextrose; soybean stalks; and alfalfa. A partial analysis of these materials is given in table 1, and the methods of preparations of the oat straw materials follow.

##### *Pretreatment of oat straw*

Inasmuch as it was intended to study the decomposition of the treated and the untreated straw both in the absence and in the presence of soil, and because finely ground straw could not be used in the former circumstance, the treatments were applied to straw that had been cut into short lengths in an ensilage cutter. That portion of the preparation required for addition to soil was later ground more finely in a Wiley mill.

*Sulfuric acid extraction of straw.* The chief purpose of this treatment was to remove the hemicelluloses and other more hydrolyzable constituents, and to leave a residue consisting primarily of cellulose and lignin. It was carried out by boiling 150 gm. of straw in 5 liters of 5 per cent sulfuric acid for 1 hour, then washing until free of acid. The loss on hydrolysis was about 40 per cent. The lignin content of the residue was 26 per cent, an increase of 53 per cent over that of the original straw.

*Chlorine, alcoholic-ethanolamine extraction of straw (23).* The purpose of this treatment was to accomplish partial delignification without concurrent removal of hemicellulose or other non-water-soluble polysaccharides.

Water was added to 250 gm. of straw and allowed to remain until the straw was wet. Then 400 ml. of sodium hypochlorite (5.25 per cent Cl) was added, and the solution was made just acid with sulfuric acid. After thorough stirring, this was allowed to stand for 15 minutes, then the solution was drained off. Sufficient hot 3 per cent alcoholic ethanolamine (3 parts of monoethanolamine added to 97 parts of 95 per cent alcohol) was added completely to cover the mate-

rial, and stirred thoroughly. This was allowed to stand 5 minutes and was then drained off. The residue was washed with cold distilled water until neutral to litmus.

This treatment brought about incomplete delignification, the content in the residue being only 6 per cent less than that of the original straw. Though it would be anticipated that the nitrogen content of the straw would be reduced by the treatment, inasmuch as proteins would be attacked by the chlorination, the apparent nitrogen content was in fact increased, probably as a result of condensation of some ethanolamine with the residual lignin. Other constituents soluble

TABLE 1  
*Composition of materials used in the decomposition studies*

MATERIAL	LOSS BY TREAT- MENT	NITRO- GEN	CAR- BON	LIGNIN	LIGNIN RE- MOVED BY TREAT- MENT	CELLU- LOSD*	FUR- FURAL- DEHYDE FROM CELLU- LOSE*	XYLAN IN CELLU- LOSE	TOTAL FUR- FURAL- DE- HYDE*	POLYURONIDE HEMI- CELLULOSE FUR- FURALDEHYDE
	%	%	%	%	%	%	%	%	%	%
Oat straw untreated..	..	0.39	43.62	17.1	....	49.6	8.2	12.7	15.6	7.4
5% H <sub>2</sub> SO <sub>4</sub> -extracted oat straw.....	40	0.25	47.01	26.3	7.9	63.0	6.0	9.4	8.6	2.6
Cl-amine-extracted oat straw.....	26	0.45	46.01	16.0	30.8	62.2	9.1	14.0	17.4	8.3
0.5% Na <sub>2</sub> CO <sub>3</sub> -ex- tracted oat straw....	29	0.27	45.93	17.2	24.7	61.8	9.5	14.7	18.3	8.8
0.5% NaOH-extracted oat straw.....	40	0.09	45.92	10.3	64.0	73.5	11.9	18.4	16.7	4.8
NaOH, NaOCl, Na <sub>2</sub> - SO <sub>3</sub> -extracted oat straw (cellulose)....	60	0.07	43.08	3.4	91.9	91.5	14.6	22.5	16.6	2.0
Thurman fine sandy loam.....	..	0.05	0.62	...	....	....	....	....	....	...
Dextrose.....	..	....	40.00	...	....	....	....	....	....	...
Soybean stalks.....	..	0.76	46.85	15.6	....	....	....	....	....	...
Alfalfa.....	..	3.54	45.70	15.8	....	....	....	....	....	...

\* Analyses by L. N. Spohnheimer.

in water and alcohol were removed, and the total loss was 25 per cent of the original.

*Sodium carbonate (0.5 per cent) extraction of straw.* This extraction was applied to accomplish extensive removal of the hemicelluloses and partial delignification.

About 150 gm. of straw was boiled in 5 liters of 0.5 per cent sodium carbonate solution for 15 minutes; then the residue was washed free of carbonate with cold distilled water. The total loss was 29 per cent.

*Sodium hydroxide (0.5 per cent) extraction of straw.* The purpose of this treatment, which was carried out by boiling 150 gm. of straw in 5 liters of 0.5 per cent

sodium hydroxide for 30 minutes, was to bring about more extensive delignification than that accomplished by the carbonate. The effect on the hemicelluloses and nitrogenous constituents would not be greatly different from that in foregoing extraction. The loss on extraction was 40 per cent, and the lignin content of the residue was only 60 per cent as high as in the original straw. The nitrogen content was only about one-fourth as high.

*"Cellulose" preparation* (15). The purpose of this treatment was to remove virtually all incrusting materials from the cell walls and to leave only that portion of the cellulose resistant to extraction by alkali. The total loss caused by the treatment was 60 per cent.

The treatments consisted first of boiling 150 gm. of straw in 5 liters of 1 per cent sodium hydroxide for 10 minutes, and washing free of hydroxide with water. The straw was then covered with water, 250 ml. of sodium hypochlorite (0.5 per cent Cl) was added, the mixture was made acid with sulfuric acid and stirred well. After 15 minutes the sodium hypochlorite and sulfuric acid treatments were repeated, the mixture was allowed to stand another 15 minutes, and was drained off.

The residue was then boiled with 3 per cent sodium sulfite for 20 minutes, drained off, and washed with distilled water until neutral. The structure of the straw was not maintained in this preparation.

#### *Soil treatments*

Twenty pots, each containing 2 kilos of Thurman soil, were set up with the addition of 10 per cent finely ground organic material in the form of oat straw, the oat straw residues from the various straw treatments, soybean stalks, alfalfa, and dextrose. All were made up to a C:N ratio of 29:1 with ammonium nitrate, except one set of soybean stalks which was left at the original ratio of 62:1, and the alfalfa which was left at 13:1. Two pots of soil were set up as checks. To each was added 6 gm. of calcium carbonate. To the pots receiving the plant residues, 900 ml. of water was added; to those receiving dextrose, 315 ml.; and to the check soils, 290 ml. Water was added regularly as needed.

#### *Decomposition of straw separate from soil*

The oat straw residues, except the "cellulose" preparation, were placed in fruit jars. Fifty grams of each material was put in a jar and made up to a C:N ratio of 29:1 with ammonium nitrate, and 175 ml. of water added. The jars, set up in triplicate, were inoculated with an extract made from the original oat straw and a soil high in organic matter.

#### *Sampling and analyses*

Each pot of soil was mixed thoroughly and sampled 105, 328, 580, and 833 days after the experiment was started. The samples were analyzed at each period in order to follow the changes taking place during decomposition.

One jar of each plant material was analyzed after 112 days; one jar after 322 days; and the last after 596 days.



In the analysis of the soil and organic materials, the official method of the A.O.A.C. (1) was used for determination of total nitrogen. Total carbon was determined by the dry combustion method (30). Base-exchange capacity was determined by the barium acetate, calcium acetate method of Millar, Smith, and Brown (13). Organic exchange capacity was derived by oxidizing the soil with  $H_2O_2$ , determining inorganic exchange capacity, then subtracting this from the total exchange capacity. Lignin was determined by the method of Norman and Jenkins (16). The hypiodite oxidations of the soils and plant materials followed a method previously reported from this laboratory (18). The hypochlorite oxidations were according to a method reported by Norman (17).

#### EXPERIMENTAL RESULTS AND DISCUSSION

##### *Effects of composition of plant residues on amount and nature of soil organic matter*

All organic materials added to the soil in this study were at first rapidly decomposed, and after 105 days from 50 to 95 per cent of the carbon added had disappeared (table 2). Except where dextrose was added, there was considerable decomposition after 105 days, but there was little after 328 days regardless of the nature of the organic material added. The oat straw "cellulose" preparation, which contained 3.4 per cent lignin, was much more rapidly and completely decomposed than any of the other additions of plant materials. After 833 days' decomposition, only 7.4 per cent of the "cellulose" preparation remained in the soil, whereas 22.6 per cent of the acid-hydrolyzed straw was still present. This latter material was the most resistant to decomposition, no doubt because of its large lignin content and the extensive removal of hemicelluloses and other more soluble constituents. The degree of decomposition of the other oat straw materials was intermediate between the "cellulose" and the acid-hydrolyzed straw, depending on the lignin content of the material and the degree of removal of cellulose and other materials by the pretreatments.

To study the nature of the residues from these materials, the soils were treated with 72 per cent sulfuric acid as in the procedure used to determine lignin, and the content of acid-resistant organic material was then determined in the soils (table 3). Wide variations were found in the percentage of acid-resistant material, but even greater variations were found in the quantities of acid-resistant material as compared to that in check soil. The total amount present in the soil which received acid-hydrolyzed straw was almost three times as great as that in the check soil and much higher than where any other material was used. It is also of interest to note that where dextrose was added, the amount of acid-resistant material was less than in the check soil, even though the total carbon present was higher in the former. This is indicative of the fact that the synthesized tissues produced under these circumstances contain little if any acid-resistant constituents. When the "cellulose" preparation was added, the increase was only about one-fourth as great as when the acid-hydrolyzed straw was added.

The quantities of nitrogen resistant to removal by this strong acid treatment in these soils were higher than in the check soil, but removal of nitrogen by this

treatment was generally more extensive than that of carbon. In all instances the C:N ratios were higher after the strong acid treatment.

TABLE 2  
*Changes in organic carbon in soil during decomposition*

ORGANIC MATERIAL ADDED TO SOIL	CARBON CONTENT				PER CENT OF ADDED CARBON LEFT AFTER 833 DAYS
	After 105 days	After 328 days	After 580 days	After 833 days	
	%	%	%	%	
Check.....	0.67	0.66	0.61	0.59	....
Oat straw untreated.....	2.04	1.36	1.21	1.13	12.4
5% H <sub>2</sub> SO <sub>4</sub> -hydrolyzed straw.....	2.65	1.72	1.72	1.65	22.6
Cl-amine-extracted straw.....	2.75	1.52	1.48	1.41	17.8
0.5% Na <sub>2</sub> CO <sub>3</sub> -extracted straw.....	2.32	1.44	1.32	1.29	15.2
0.5% NaOH extracted straw.....	2.25	1.35	1.21	1.17	12.6
"Cellulose" from oat straw.....	1.46	1.23	1.11	0.91	7.4
Dextrose.....	0.83	0.76	0.71	0.70	2.8
Alfalfa.....	2.30	1.41	1.34	1.30	15.6
Soybeans 62/1 C:N.....	2.91	1.33	1.27	1.22	13.5
Soybeans 29/1 C:N.....	3.35	1.35	1.34	1.22	13.5

TABLE 3  
*Effect of 72 per cent H<sub>2</sub>SO<sub>4</sub> on carbon and nitrogen contents of soil after decomposition for 833 days*

ORGANIC MATTER ADDED TO SOIL	CARBON		NITROGEN		C/N RATIOS		RESISTANT MATERIAL IN SOIL ORGANIC MATTER	INCREASE IN ACID-RESISTANT MATERIAL IN SOIL
	Before acid treatment	After acid treatment	Before acid treatment	After acid treatment	Before acid treatment	After acid treatment		
	%	%	%	%			%	%
Check.....	0.58	0.39	0.067	0.034	8.7	11.5	67	....
Oat straw untreated...	1.19	0.71	0.119	0.066	10.0	10.8	60	82
5% H <sub>2</sub> SO <sub>4</sub> -hydrolyzed straw.....	1.50	1.15	0.145	0.073	10.3	15.8	72	194
Cl-amine-extracted straw.....	1.46	0.84	0.132	0.069	11.1	12.2	58	115
0.5% Na <sub>2</sub> CO <sub>3</sub> -extracted straw.....	1.34	0.89	0.127	0.074	10.6	12.0	66	128
0.5% NaOH-extracted straw.....	1.15	0.80	0.131	0.057	8.8	14.0	70	106
"Cellulose" from oat straw.....	0.93	0.59	0.101	0.055	9.2	10.7	63	51
Dextrose.....	0.71	0.38	0.103	0.043	7.9	8.8	54	-2.5
Alfalfa.....	1.29	0.82	0.156	0.094	8.3	8.7	64	110
Soybean 62/1 C:N.....	1.21	0.71	0.123	0.070	9.8	10.1	59	82
Soybean 29/1 C:N.....	1.26	0.70	0.135	0.069	9.3	10.1	56	80

These differences in the residues can be attributed only to differences in composition of the organic materials added. Some fraction of these materials was

less susceptible to decomposition than others. Since lignin was the constituent that varied most widely in amount and since the materials that were at least extensively decomposed were those that were highest in lignin, it is deduced that lignin was largely responsible for this resistance to decomposition and for the increased amount of acid-resistant material present in the residues.

The decomposition of these plant materials in the absence of soil also showed that those high in lignin were more resistant to decomposition by microorganisms (table 4). These materials with a high lignin content were decomposed much more thoroughly when incorporated in soil. This is most likely due to the population differences in the two environments. Organisms that can perhaps bring

TABLE 4  
*Decomposition of plant materials in absence of soil*

PLANT MATERIAL	DECOMPOSITION		
	After 112 days	After 322 days	After 596 days
	%	%	%
Oat straw untreated.....	47.4	73.8	77.2
5% H <sub>2</sub> SO <sub>4</sub> -hydrolyzed straw.....	5.3	29.4	18.4
Cl-amine-extracted straw.....	8.0	28.0	31.9
0.5% Na <sub>2</sub> CO <sub>4</sub> -extracted straw.....	19.9	41.6	52.0
0.5% NaOH-extracted straw.....	12.4	46.4	77.8

TABLE 5  
*Apparent lignin content of plant materials during decomposition in absence of soil*

PLANT MATERIAL	APPARENT LIGNIN CONTENT			
	At beginning	After 112 days	After 322 days	After 596 days
	gm.*	gm.*	gm.*	gm.*
Oat straw untreated.....	17.1	15.0	9.3	8.2
5% H <sub>2</sub> SO <sub>4</sub> -hydrolyzed straw.....	26.3	25.3	25.3	22.5
Cl-amine-extracted straw.....	16.0	17.5	17.6	17.2
0.5% Na CO <sub>4</sub> -extracted straw.....	17.2	17.7	17.9	15.2
0.5% NaOH-extracted straw.....	10.3	11.6	13.7	14.1

\* Per 100 gm. original material.

about a slow attack on lignified tissues in the soil may be unadapted to the highly aerobic, drier conditions in the jars. The amount of apparent lignin remaining in these materials after 596 days of decomposition also helps to emphasize the resistance of this constituent to destruction by microorganisms (table 5). Even though the untreated straw was 77 per cent decomposed at this time, only about half of the lignin therein was destroyed and only a small amount of the lignin in any other material was decomposed. The apparent lignin content of the Cl-amine-treated straw increased slightly, and that of the sodium-hydroxide-extracted straw increased considerably. The increase in the latter material is attributed to synthesized products formed during the decomposition process. In the Cl-

amine-treated straw, this increase may be due in part to the effects of the amine treatment. There is an indication in the increase in the nitrogen content of the residue after the Cl-amine treatment (table 1) that some combination between amine and lignin may have taken place.

It has been reported by other workers that lignin is of great importance in soil organic matter. Fischer (7) demonstrated that in the formation of peat the celluloses of plant residues change to  $\text{CO}_2$  and water, whereas the lignin accumulates, even though it may be altered somewhat. In the work reported here, it was found, with one exception, that part of the lignin was decomposed but not to the same degree as cellulose and other constituents. Wehmer (29) also reported that lignin was attacked less than other constituents and believed that it was converted into humic acids. Similar results have been reported by Rose and Lisse (20) and others (3, 24, 25).

Even though decomposition of the oat straw preparations was slow after 833 days, it could not be considered to have stopped completely, and part of the lignin was definitely decomposed. Several workers (12, 21, 22) have reported rather large losses of lignin over periods of several months, and Phillips (19) has concluded that, under proper conditions, soil organisms are capable of decomposing lignin in plant materials and, under suitable conditions, the rate of decomposition may be as great as that of cellulose and pentosans. This latter statement was not found to be true for the extracted lignified materials in this study.

#### *Exchange studies*

Further information on the nature of the residues from these materials was brought out by studies on total exchange and organic exchange capacities (table 6). The total exchange capacities were highest in the soils receiving the plant materials high in lignin, but the results are more striking when the increases in organic exchange capacities are considered. At the end of the experiment the soils receiving the materials high in lignin had organic exchange capacities almost three times as great as that of the check soil, whereas the soil receiving the "cellulose" preparations had an increase only one-fourth as great. However, increases in exchange capacities, like other properties, were not proportional to increases in lignin content of the original material, partly because of differences in the nature of the decomposition and the residues, caused by pretreatment of the straw.

These relatively large increases in exchange capacities are believed to be caused largely by the lignin. According to Mitchell (14), the "lignin-humus" fraction is the most important fraction of soil organic matter possessing exchange properties, since it appears to give the organic matter its more or less permanent exchange properties. McGeorge (9, 10) has said that the exchange property of organic matter is, for the most part, due to lignin compounds. Bartlett and Norman (2) found that lignin isolated from residues of different plants possessed very different exchange properties, and after decomposition for 6 months, the exchange capacities of the lignin fractions were found to have been increased severalfold. This indicates that lignin in soil organic matter becomes more active after decomposition has taken place.

The exchange capacities of the straw preparations decomposed in the absence of soil (table 7) were variable. Here again, they were not directly related to the lignin or apparent lignin contents. The more extensively decomposed materials had by far the greatest capacities per unit of residue. The differences are not so great, when the exchange capacities are calculated on the basis of 100 gm. of the

TABLE 6  
*Exchange capacity of soil and of organic matter during decomposition*  
(m.e. Ba per 100 gm. soil)

ORGANIC MATERIAL ADDED TO SOIL	TOTAL EXCHANGE CAPACITY OF SOIL				ORGANIC EXCHANGE CAPACITY OF SOIL			
	After 105 days	After 328 days	After 580 days	After 833 days	After 105 days	After 328 days	After 580 days	After 833 days
Check.....	8.0	7.9	8.3	8.3	2.1	2.0	2.3	2.3
Oat straw untreated.....	11.3	10.9	13.3	12.8	5.3	5.0	7.4	6.8
5% H <sub>2</sub> SO <sub>4</sub> -hydrolyzed straw.....	11.1	11.5	12.3	12.3	5.2	5.5	6.3	6.4
Cl-amine-extracted straw..	10.7	12.7	12.2	11.2	4.7	6.7	6.2	5.3
0.5% Na <sub>2</sub> CO <sub>3</sub> -extracted straw.....	11.4	12.1	13.1	12.0	5.4	6.2	7.1	6.0
0.5% NaOH-extracted straw.....	9.4	11.2	11.1	10.3	3.4	5.3	5.1	4.3
"Cellulose" from oat straw.....	9.2	10.6	9.9	9.6	3.3	4.6	3.9	3.6
Dextrose.....	8.4	8.7	9.3	9.8	2.4	2.7	3.4	3.8
Alfalfa.....	10.0	12.6	12.9	12.8	4.1	6.6	7.0	6.8
Soybeans 62/1 C:N.....	11.4	11.6	11.8	11.7	5.4	5.8	5.8	5.7
Soybeans 29/1 C:N.....	11.2	12.1	11.7	11.7	5.3	6.1	5.8	5.8

TABLE 7  
*Base exchange capacity of plant materials during decomposition in absence of soil*

PLANT MATERIAL	ORIGINAL MATERIAL (M.E. Ba PER 100 GM.)				RESIDUAL MATERIAL (M.E. PER 100 GM.)		
	At beginning	After 112 days	After 322 days	After 596 days	After 112 days	After 322 days	After 596 days
Oat straw untreated.....	42.3	60.1	58.8	51.4	114.3	224.8	225.0
5% H <sub>2</sub> SO <sub>4</sub> -hydrolyzed straw.....	34.8	27.9	26.4	29.0	29.5	37.4	35.5
Cl-amine-extracted straw.....	34.3	28.1	23.8	25.0	30.6	33.0	36.7
0.5% Na <sub>2</sub> CO <sub>3</sub> -extracted straw.....	42.3	41.9	37.7	38.7	52.3	64.6	80.8
0.5% NaOH-extracted straw.....	32.9	34.5	22.8	23.1	39.5	42.5	104.0

original material (table 7). It was found, on this basis, that all except one of the materials had decreased exchange capacities after 596 days. Therefore, even though the residues were more active, it is evident that some material having exchange properties was being decomposed, and faster than the increase in the activity of the residues.



*Nitrogen relationships*

As the decomposition of the plant materials proceeded and the carbon content decreased, the amount of nitrogen in the soils in all treatments also decreased materially (table 8), though not to the same extent as the carbon. The soil receiving the dextrose showed the greatest decrease in nitrogen, most of which occurred in 105 days, whereas the soil receiving the acid-hydrolyzed straw showed the smallest decrease. The soils contained only relatively small amounts of nitrate nitrogen or ammonia nitrogen at any time and since there were no losses from leaching and none from plant removal, the only loss was into the atmosphere.

Because of this decrease in nitrogen content as decomposition proceeded, the conclusion might be drawn that nitrogen was conserved only because of the resistance of the different materials to decomposition. Upon closer observation,

TABLE 8  
*Total nitrogen in soil during decomposition*

ORGANIC MATERIAL ADDED TO SOIL	NITROGEN CONTENT			
	After 105 days	After 328 days	After 580 days	After 833 days
	%	%	%	%
Check.....	0.067	0.058	0.058	0.067
Oat straw untreated.....	0.172	0.146	0.134	0.119
5% H <sub>2</sub> SO <sub>4</sub> -hydrolyzed straw.....	0.167	0.161	0.147	0.140
Cl-amine-extracted straw.....	0.161	0.147	0.142	0.130
0.5% Na <sub>2</sub> CO <sub>3</sub> -extracted straw.....	0.173	0.152	0.136	0.130
0.5% NaOH-extracted straw.....	0.152	0.128	0.118	0.132
"Cellulose" from oat straw.....	0.144	0.112	0.104	0.099
Dextrose.....	0.106	0.092	0.097	0.090
Alfalfa.....	0.240	0.202	0.176	0.160
Soybeans 62/1 C:N.....	0.136	0.158	0.133	0.122
Soybeans 29/1 C:N.....	0.159	0.168	0.130	0.134

however, other factors influencing the conservation of nitrogen may be pointed out. The nitrogen contents decreased materially, as evidenced by the C:N ratio, but not so rapidly as the materials decomposed (table 9). It may be concluded, therefore, that nitrogen was conserved by the partly decomposed residues, probably as microbial tissue. If this were not true, the C:N ratios would have been much wider as decomposition proceeded. After 833 days the ratios varied from 8.8:1 to 11.8:1, the latter being in the soil to which acid-hydrolyzed straw had been added. This soil also had a higher percentage of total nitrogen than any of the others receiving oat straw preparations.

Waksman and Hutchings (26) reported that lignin is important in nitrogen conservation, acting as a buffer for the adsorption of ammonia. This was not true in this study, for but little ammonia was present at any time. They said also that lignin "fixes" protein in the form of lignoprotein complexes and thus helps to keep the nitrogen content of soil at a higher level. This seems to have been true in this work, for soils receiving materials high in lignin had much greater nitrogen supplies finally than did those receiving dextrose, "cellulose," or other

oat straw preparations low in lignin, although the nitrogen levels of all were identical initially. The nitrogen conservation, however, was not proportionate to the lignin content, probably because increased activity of the lignin in the highly decomposed materials formed more ligno-protein complexes. Large losses of nitrogen occurred when the materials were decomposed in the absence of soil (table 10), though the nitrogen content of some of the residues after 596 days was high, particularly in the untreated straw, which was extensively decomposed.

TABLE 9  
*Carbon: nitrogen ratios of soil during decomposition*

ORGANIC MATERIAL ADDED TO SOIL	CARBON: NITROGEN RATIO			
	After 105 days	After 328 days	After 580 days	After 833 days
Check.....	10.1	11.1	10.4	8.8
Oat straw untreated.....	11.8	9.3	9.0	9.5
5% H <sub>2</sub> SO <sub>4</sub> -hydrolyzed straw.....	15.9	10.7	11.7	11.8
Cl-amine-extracted straw.....	17.1	10.4	10.4	10.9
0.5% Na <sub>2</sub> CO <sub>3</sub> -extracted straw.....	14.0	9.2	9.7	10.0
0.5% NaOH-extracted straw.....	14.8	10.5	10.3	8.8
"Cellulose" from oat straw.....	10.1	11.0	10.7	9.7
Dextrose.....	7.8	8.4	7.3	7.9
Alfalfa.....	9.6	7.0	7.6	8.1
Soybeans 62/1 C:N.....	21.4	8.4	9.5	10.0
Soybeans 29/1 C:N.....	21.1	8.1	10.3	9.0

TABLE 10  
*Changes in total nitrogen content during decomposition of plant materials in absence of soil*

PLANT MATERIAL	NITROGEN CONTENT			ORIGINAL N ACCOUNTED FOR AFTER 596 DAYS*
	After 112 days	After 322 days	After 596 days	
	%	%	%	%
Oat straw untreated.....	1.97	2.80	3.82	55
5% H <sub>2</sub> SO <sub>4</sub> -hydrolyzed straw.....	1.25	1.45	1.12	56
Cl-amine-extracted straw.....	1.18	1.29	1.36	49
0.5% Na <sub>2</sub> CO <sub>3</sub> -extracted straw.....	1.28	1.54	1.82	54
0.5% NaOH-extracted straw.....	1.10	1.68	2.02	27

\* Original N = N in plant material plus N added as NH<sub>4</sub>NO<sub>3</sub>.

The lignin contents of the chemically extracted straw preparations were higher than in the untreated straw, but the protein content was higher in the latter because of greater microbial synthesis and greater formation of lignoprotein complexes.

#### *Oxidation studies*

Application of hypochlorite and hypiodite oxidative procedures to the treated soils and decomposed plant residues obtained in these investigations permits of an evaluation of the suitability of these methods in following changes in the com-

position of decomposing plant materials, or in comparing the organic matter of soils. The methods were devised on the grounds that changes in amounts of those constituents susceptible to oxidation could readily be followed.

The results of the oxidation of the soils and the straw materials show that these procedures may be used to throw light on the nature of the soil organic matter but not on the quantity, if there are variations in the nature of the material. This is true because certain constituents of organic matter are more susceptible than others to oxidation by these reagents. Lignin has been found to be the major plant constituent most susceptible to these oxidations. Protein is also oxidized by these reagents but to a lesser extent than lignin. Therefore, the extent of oxidation of organic matter by these reagents will be determined largely by the lignin and protein contents of the materials and by the extent and nature of their decomposition.

TABLE 11  
*Hypiodite oxidation of soil during decomposition*  
(m.e. I<sub>2</sub> per 100 gm. soil)

ORGANIC MATERIAL ADDED TO SOIL	OXIDATION OF SOILS			
	After 105 days	After 328 days	After 580 days	After 833 days
Check.....	3.90	3.90	4.80	4.50
Oat straw untreated.....	15.35	8.85	10.10	11.65
5% H <sub>2</sub> SO <sub>4</sub> -hydrolyzed straw.....	25.50	16.05	20.00	19.55
Cl-amine-extracted straw.....	17.60	11.25	12.65	13.95
0.5% Na <sub>2</sub> CO <sub>3</sub> -extracted.....	19.45	9.85	10.85	13.80
0.5% NaOH-extracted straw.....	15.90	7.60	8.40	11.55
"Cellulose" from oat straw.....	15.20	8.40	8.00	9.55
Dextrose.....	13.65	6.20	6.35	6.75
Alfalfa.....	15.50	9.00	10.10	12.95
Soybeans 62/1 C:N.....	13.55	6.60	8.70	8.40
Soybeans 29/1 C:N.....	12.95	7.60	8.85	8.40

It was found that the organic matter in the soils receiving the high lignin materials was more susceptible to hypiodite oxidation than was that in the soils receiving the materials low in lignin (table 11). The soil receiving the acid-treated straw was more than four times as active toward this reagent as the check soil. The carbon content was less than three times as great, showing that the organic matter in the soils receiving the acid-hydrolyzed straw was more oxidizable than that in the check soil, as shown by the I<sub>2</sub>:C ratio in table 12. The same general relation was shown by oxidizing the soils that were treated with 72 per cent sulfuric acid (table 13). The I<sub>2</sub>:C ratios for the materials with relatively high lignin contents were fairly constant and were higher than the ratios for the check soil and soils receiving materials low in lignin.

The results of the hypiodite oxidation of the decomposed straw material (table 14) show that the residues were generally more highly oxidizable as decomposition proceeded and as the lignin content increased. The apparent lignin

TABLE 12  
*Iodine: carbon ratios of soil during decomposition*

ORGANIC MATERIAL ADDED TO SOIL	M.E. I <sub>2</sub> : TOTAL CARBON RATIO			
	After 105 days	After 328 days	After 580 days	After 833 days
Check.....	5.82	5.97	7.90	7.63
Oat straw untreated.....	7.57	6.54	8.41	10.37
5% H <sub>2</sub> SO <sub>4</sub> -hydrolyzed straw.....	9.94	9.37	11.62	11.84
Cl-amine-extracted straw.....	6.41	7.42	8.55	9.87
0.5% Na <sub>2</sub> CO <sub>3</sub> -extracted straw.....	8.48	6.84	8.20	10.64
0.5% NaOH-extracted straw.....	7.12	5.65	6.98	9.85
"Cellulose" from oat straw.....	10.46	6.83	7.25	10.50
Dextrose.....	16.50	8.16	8.97	9.04
Alfalfa.....	8.75	6.40	7.56	9.95
Soybeans 62/1 C:N.....	4.64	5.06	6.89	6.92
Soybeans 29/1 C:N.....	3.87	5.65	6.61	6.95

TABLE 13  
*Hypoiodite oxidation of 72 per cent sulfuric-acid extracted soil after decomposition for 833 days*

ORGANIC MATTER ADDED TO SOIL	M.E. I <sub>2</sub> PER 100 GM. SOIL		M.E. I <sub>2</sub> /C	
	Before acid treatment	After acid treatment	Before acid treatment	After acid treatment
Check.....	4.50	3.09	7.76	7.91
Oat straw untreated.....	11.81	8.16	9.92	11.5
5% H <sub>2</sub> SO <sub>4</sub> -hydrolyzed straw.....	19.69	12.38	13.13	10.74
Cl-amine-extracted straw.....	14.35	9.87	9.8	11.67
0.5% Na <sub>2</sub> CO <sub>3</sub> -extracted straw.....	13.05	9.56	10.07	10.74
0.5% NaOH-extracted straw.....	11.25	9.20	9.78	11.5
"Cellulose" from oat straw.....	10.12	5.14	10.88	8.71
Dextrose.....	6.47	3.09	9.11	8.13
Alfalfa.....	12.37	8.84	9.74	10.78
Soybeans 62/1 C:N.....	8.44	7.34	6.98	10.34
Soybeans 29/1 C:N.....	8.44	7.31	6.77	10.44

TABLE 14  
*Hypoiodite oxidation of straw during decomposition in absence of soil  
(m.e. I per 100 gm.)*

PLANT MATERIAL	RESIDUAL MATERIAL			ORIGINAL MATERIAL		
	After 112 days	After 322 days	After 596 days	After 112 days	After 322 days	After 596 days
Oat straw untreated.....	231	284	236	121.6	73.2	53.7
5% H <sub>2</sub> SO <sub>4</sub> -hydrolyzed straw.....	245	340	290	232.0	240.0	192.6
Cl-amine-extracted straw.....	155	160	197	142.6	115.2	134.1
0.5% Na <sub>2</sub> CO <sub>3</sub> -extracted straw.....	186	211	228	149.1	128.2	109.4
0.5% NaOH-extracted straw.....	183	211	318	160.3	113.0	70.5

content of the sodium-hydroxide-treated straw was very high at the end of the experiment, and this residue was very highly oxidizable by hypiodite.

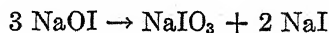
It seems, from these data, that the hypiodite oxidation is closely related to the lignin content of the residues. When these residues are derived from the same source, variation in oxidation values will be due largely to differences in lignin content of the residues; but when the residues are derived from different materials, variations in oxidation values will probably be due to differences in the nature of the lignin as well as its content.

It is also of interest to note the amount of iodine utilized per 100 gm. soil before and after the strong acid treatment. In the soils receiving the materials high in lignin, the values after acid treatment were about two-thirds as large as before, whereas soils receiving dextrose and "cellulose" had values only one-half as large after acid treatment as before. This indicates that there was a difference in the nature of these residues, the former group probably being higher in lignin than the latter, and that present in the former group being more susceptible to oxidation. That the lignin was more active was brought out by the  $I_2:C$  ratios after acid treatment.

In previous work reported from this laboratory (18), wide variations in hypiodite oxidation were found for the organic carbon in different soils, as well as for various depths in the same soil. These variations may be due to differences in the amount or nature of lignin, when two soils are studied, but when such a study is in the different layers of the same soil the variations are probably due to the greater percentage of lignin in the organic matter of the more active layer.

Bartlett and Norman (2) reported an average of 27 m. e. iodine utilized per gram of lignin carbon for a number of lignin preparations. The reactivity of the residues obtained in this work was lower than might have been expected on the basis of the known lignin contents, and as already suggested, there seems to be some form of combination between lignin and other constituents as a result of which the reactivity of the lignin component is reduced (18). Even after strong acid treatment, however, the material remaining in the soils did not approach the figures given for lignin directly isolated from undecomposed plant materials.

The degree of oxidation by hypiodite is limited because of the nature of this reagent as an oxidant. When iodine is added to sodium hydroxide with the formation of hypiodite, the reaction



begins and proceeds rapidly at ordinary temperatures so that at the end of 20 to 30 minutes no free hypiodite remains. When an oxidizable material is treated with this reagent, the oxidation of the material will end when the foregoing reaction had ended, even though much of the material may still be susceptible to further oxidation.

The hypochlorite oxidation (tables 15 and 16) is far more extensive than that of the hypiodite, chiefly because of the difference between the two reagents. In contrast to hypiodite oxidation, hypochlorite oxidation is initially more active



and may continue for several days though the rate is much reduced after 18 to 14 hours.

In this work, the hypochlorite oxidation seemed to be related more closely to the nitrogen than to the lignin content, but this was not definitely established. At the end of the experiment the oxidation values for the untreated straw and the NaOH-extracted straw were about the same, yet the former material was much higher in organic nitrogen than the latter. The latter, however, had a

TABLE 15  
*Hypochlorite oxidation of soils during decomposition*  
(m.e. Cl per 100 gm. soil)

ORGANIC MATERIAL ADDED TO SOIL	OXIDATION OF SOILS			
	After 103 days	After 328 days	After 580 days	After 833 days
Check.....	44.5	50.0	40.6	43.0
Oat straw untreated.....	198.0	129.5	132.5	168.5
5% H <sub>2</sub> SO <sub>4</sub> -hydrolyzed straw.....	248.0	190.0	158.7	168.5
Cl-amine-extracted straw.....	207.4	164.5	134.4	147.5
0.5% Na <sub>2</sub> CO <sub>3</sub> -extracted straw.....	188.0	146.5	133.3	151.4
0.5% NaOH-extracted straw.....	161.2	130.0	108.2	121.7
"Cellulose" from oat straw.....	119.5	101.5	81.8	76.9
Dextrose.....	91.5	70.5	59.7	64.3
Alfalfa.....	199.0	149.0	132.2	122.6
Soybeans 62/1 C:N.....	187.0	146.0	89.1	102.7
Soybeans 29/1 C:N.....	172.5	143.0	104.0	104.5

TABLE 16  
*Hypochlorite oxidation of straw during decomposition in absence of soil*  
(m.e. Cl per 100 gm. straw)

PLANT MATERIAL	RESIDUAL MATERIAL			ORIGINAL MATERIAL		
	After 112 days	After 322 days	After 596 days	After 112 days	After 322 days	After 596 days
Oat straw untreated.....	2670	3460	3067	1405	905	700
5% H <sub>2</sub> SO <sub>4</sub> -hydrolyzed straw.....	1750	2360	1616	1657	1666	1319
Cl-amine-extracted straw.....	1690	1800	1468	1555	1296	1000
0.5% Na <sub>2</sub> CO <sub>3</sub> -extracted straw.....	1850	2220	2027	1482	1297	1271
0.5% NaOH-extracted straw.....	1110	1830	3029	972	980	672

much greater apparent lignin content, and since lignin is also extensively oxidized by hypochlorite, it was probably this greater amount of lignin that caused the total oxidation value to be as large as that for the untreated straw. The oxidation of the other residues followed fairly closely the protein content, and here, too, the variation was probably caused, at least in part, by the variations in the amount and nature of the lignin.

Norman (17) reported that there was an accumulation of lignin and nitrogenous complexes during aerobic decomposition processes, and that these were

particularly susceptible to oxidation by hypochlorite. He found no clear evidence for a change in reactivity of the lignin during decomposition, but believed that the increase in reactivity might be taken as a measure of the accumulation of lignin and nitrogenous complexes. He suggested that this reagent might be used to study the residues from the same parent substance, but probably would not be suitable for comparison of residues of different sources and types, mainly because of the differences in reactivity and behavior of the lignin contained. The same general conclusions are reached from the work reported here.

Hypochlorite, because of the duration of the oxidation, would be less desirable than hypiodite for studying the nature of organic matter. The activity of the latter reagent also seems to be more highly related to the lignin content than the former reagent, and for this reason, too, hypiodite is of greater value as an aid in studying the nature of organic materials.

#### SUMMARY

Effects of composition of plant materials on properties of the decomposed residues have been studied by decomposing several plant materials of known composition, both in soil and in absence of soil, and analyzing the residues at several intervals over a period of 833 days, in order to follow as closely as possible the changes taking place during decomposition.

The composition of plant materials was ascertained to influence materially the quantity and the properties of the decomposed residues. Materials high in lignin were found to be much less decomposed than materials low in lignin, even after 28 months of decomposition.

The more active residues were also those derived from parent materials with a high lignin content. Oat straw cellulose and dextrose were found to decompose rapidly, and the residues from these materials were only slightly resistant to extraction by strong sulfuric acid in the cold, indicating that there was little, if any, lignified material in these residues; whereas there was considerable increase in this acid-resistant residue in soils receiving materials high in lignin.

The nitrogen content was maintained at a higher level in soils receiving the more resistant materials. This was probably due to the formation of lignoprotein, or some other complexes, because very little nitrogen was present in the form of ammonia or nitrate.

The fraction of the exchange capacity due to organic matter in these soils varied from 28 per cent in the check soil to 50 per cent in the soils receiving plant materials high in lignin. However, the increases in exchange capacities were not proportional to the increases in lignin content of the original materials, because of differences in the amount and nature of the decomposition and of the residues brought about by the pretreatments to which the straw was subjected.

The use of hypiodite or hypochlorite as an aid in the study of the nature of soil organic matter was investigated. The activity of each reagent seems to be related to the lignin content; the latter agent also attacks the proteins.

Lignin seems to be more susceptible to oxidation by hypiodite than by hypochlorite. For this reason, and because the oxidation by hypiodite is complete

in about 20 minutes, whereas the oxidation by hypochlorite may continue for days, the former reagent would be more suitable for studying the nature of soil organic matter. Alkaline hypoiodite may be helpful in detecting differences in the nature of organic matter in soils, as well as in the various layers of the same profile, particularly where the differences are likely to be due to the nature of the vegetation from which the organic matter was derived.

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## CHEMISTRY OF THE PHOSPHATE ION IN SOIL SYSTEMS

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Interpretations of phosphate behavior in soils involve some of the most interesting and baffling problems in the domain of soil science. This is largely owing to the diversity of types of aggregate in which phosphate ion occurs and the variety of associated complexes which affect the solubility of the phosphate carrier.

As Cameron pointed out years ago (6),

... there is no class of inorganic compounds presenting so many apparent anomalies and at the same time having such importance in both pure and applied chemistry. But as voluminous and perplexing as is the chemical literature, and undoubtedly in large measure because of it, the agricultural literature of the phosphates far surpasses it in both respects, utterly defying attempts to systematize or rationalize the enormous numbers of observations recorded ...

The same author drew particular attention to the fact that calcium compounds are unstable in contact with water (which we must suppose always to be present in producing soils) and give solutions in which the ratio of phosphate to calcium is greater than in the originating solid phase. Cameron, with some cause, apparently regarded calcium phosphate as the prototype of the naturally occurring phosphates in soils, and suggested that this is a *solid solution* easily susceptible of being changed into dicalcium and monocalcium phosphate in contact with soil water. Inasmuch, however, as these latter compounds are in turn readily hydrolyzable in aqueous systems, there seems little point in emphasizing their transitory existence. Moreover, the very restricted conditions essential for preparing *any definite molecular species* from calcium and phosphate, *in vitro*, suggest that the calcium-phosphate carriers of soils have no *characteristic* ratio of calcium to phosphate.

On first impression it would appear that the release of phosphate ions from such a complex should be entirely a matter of its specific solubility (or hydrolyzability) in water modified by  $H^+$  and other ions, particularly  $Ca^{++}$ . But this is not necessarily the case, inasmuch as such complexes, upon aging, after their initial formation, tend to convert into definite mineral (not molecular) species, which can hardly be said to possess specific solubility, since they do not dissolve as a unit. The solution of phosphate from such minerals appears to be largely a matter of the surface exposed, at least over short periods.

Earl Stadtman, working under the writer's direction, and using ground apatite varying in average particle size from 0.5 mm. to 0.049 mm. diameter with very dilute HCl (pH 3.29), demonstrated that the phosphate dissolved from equal weights of material is an inverse function of particle size or is directly proportional to their relative surfaces. The time of contact between mineral particles and solvent in these experiments was about as short as possible to ensure thor-



ough mixing, actually 10 seconds, plus the time necessary to filter, approximately 2 minutes. This procedure could hardly represent true equilibrium, although we have observed that the amounts of phosphate dissolved do not increase greatly over much more prolonged periods. As Stadtman reports,

It is doubtful if a true equilibrium is ever established between an apatite crystal and dilute acids, since if the ratio of apatite to acid is low, all of the apatite will go into solution, and if the ratio is high the hydrolysis of calcium will modify the pH of the solution so that further solution of phosphate is inhibited and more or less calcium phosphate is precipitated. In other words the crystalline mineral has no specific solubility.

It thus seems probable that the size (surface) of the phosphate-carrying particles is the most important factor in determining phosphate solubility in soils in the immeasurably short time involved in the transfer of such ions from the solid to the liquid phase or to a plant root surface.

The low solubility of phosphate complexes and minerals is the cause of the low phosphate content of the soil solution in many soils, but particularly is this so in soils of arid and semiarid regions having a high content of labile calcium and high pH values. Even in regions where the soils are naturally low in calcium and pH, but where, because of this, they frequently receive large applications of lime or other calcium compounds, studies of the reactions and solubilities of calcium-phosphate complexes are of more than academic interest, and justify the emphasis placed upon them.

#### IRON AND ALUMINUM PHOSPHATES

Definite molecular species of iron phosphate probably never exist in soils, and similar compounds of aluminum must be rare because of the "weakness" of those ions considered as bases. Their behavior at the pH values within the range characteristic of soils is well shown in the work of Teakle (11). In iron phosphate, hydrolysis begins at about pH 3, and more and more phosphate enters solution as the pH rises. Aluminum phosphate manifests the same type of behavior, but hydrolysis is not substantial at pH values much below 6. Both of these compounds *if present* could therefore furnish substantial quantities of phosphate to the soil solution of neutral and alkaline soils, and the iron compound could also do so in acid soils.

Mattson's extensive experiments indicate a similar behavior in mixtures of colloidal suspensions of hydrated oxides of iron and aluminum with phosphate solutions, in that phosphate is released to solution from aggregates thus formed as the solutions become more alkaline<sup>1</sup>. This type of behavior, it will be noted, is the converse of that manifested by calcium-phosphate types, where acidity, as such, always tends to dissolve phosphate.

#### KAOLINITE AND HYDROUS ALUMINUM SILICATES

It is now generally recognized that there are many soils in which the calcium-phosphate type of complex does not play a dominant role as a source of phosphate

<sup>1</sup> Such aggregates do not release phosphate to acids (containing no adsorbable anion) except at pH values below those possible in soils, when of course the entire aggregate may dissolve.

ions to soil solution and plant. In addition to the types of colloidal precipitates studied by Mattson, it appears that kaolinite and other hydrous aluminum silicates of similar crystalline structure are capable of holding phosphate against the reagent (hydrochloric acid) which has proved most useful in studying soils dominated by the calcium-phosphate type of complex. Moreover the presence of kaolinite in soils affects the interpretation of solubility data obtained with acids, in that part or all of the phosphate dissolved is adsorbed *pari passu* by the clay mineral and cannot be found in the resulting solutions. This effect was experimentally demonstrated in a previous paper by the writer (4).

Extensive experiments by Murphy (9), in this laboratory, have disclosed the conditions which must obtain for the adsorption or release of phosphate from finely ground kaolinite. He also demonstrated that soils known to contain substantial quantities of kaolinite exhibit a similar type of behavior. Stout (10), in a critical study of kaolinite and related soil minerals has demonstrated that the type of behavior manifested is a necessary consequence of their crystal structure.

#### TYPES OF BEHAVIOR IN RESPECT TO PHOSPHATE SOLUBILITY IN SOILS

The results of these studies, and a multiplicity of other data now at hand, warrant the opinion that the potential phosphate solubility of individual soils can best be studied by ascertaining the amounts of phosphate dissolved throughout the entire range of pH characteristic of soil, that is, from pH 3 to 9. The first fruit of such studies is to show whether or not the soil is dominated by the calcium-phosphate type of complex, on the one hand, or by that of the kaolinitic minerals and/or hydrous oxides of iron and aluminum, on the other.

Figure 1 shows the patterns of the two types of behavior.<sup>2</sup> The phosphate dissolved is plotted against the pH values of the solutions and not against those of the acid or alkali used.

The relatively high figures, shown in both types, for phosphate in the most alkaline solutions are due partly to humus, as such solutions are always dark or black in color, but as would be expected, the values at those pH's tend to be higher for the kaolinitic than for the calcium-phosphate type of soil.

The general characteristics of these curves always appear in extreme examples of the two types and can usually be identified in intermediate types.

In the calcium type, although the pattern of the curve is always followed, the absolute values for phosphate vary over a considerable range on the acid side and tend to be coordinated with the pH values of the resulting solutions more nearly than with those of the solutions used. The pH values of the resulting solutions are, of course, determined by the so-called "buffering" power of the particular soil and the solubility of the other minerals therein.

<sup>2</sup> The writer is aware that his use of the term "calcareous" does not conform to the definition of calcareous soils given in soil classifications, in that its use is not restricted to soils containing calcium carbonate. We have been unable, however, to find a better term to describe the vast number of soils containing substantial amounts of exchangeable calcium and limited amounts of kaolinite or hydrated oxides of iron and aluminum, in which calcium plays a dominant role in determining phosphate solubility.

In soils of the kaolinitic type the pattern can always be identified and the absolute amounts of phosphate represented are so low that such relative variations as are found to occur can hardly be regarded as significant. Of the soils we have studied which fall in this category, and in which plants have been grown, with and without phosphate, *all require phosphate fertilization* to give normal plants or normal yields and testify to the practical significance of their classification into this group.

Soils in the calcium-phosphate category *may or may not* require phosphate fertilization. The significance of such data in this respect is reserved for later discussion.

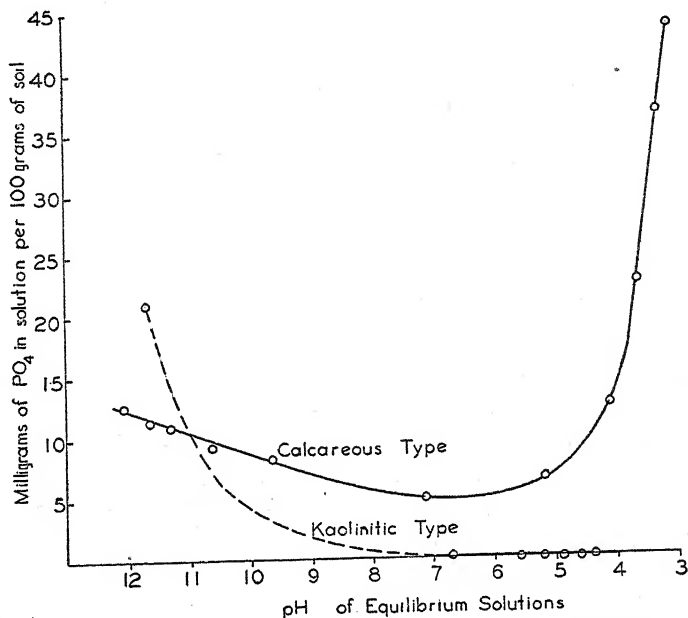


FIG. 1. TYPES OF BEHAVIOR IN RESPECT TO PHOSPHATE SOLUBILITY IN SOILS  
Phosphate in 1:5 equilibrium extracts. Concentrations of HCl used, 0.002, 0.004, 0.006, and 0.01 N; concentration of NaOH, 0.10 N.

#### EVIDENCE FROM SOIL SOLUTION STUDIES

In our earlier development of water displacement of soils (2) primary concern was in establishing, more firmly, the validity of the soil solution concept, as such. It was also hoped that solutions so obtained might give valuable indications of the supplying power of particular soils to plants. These aims have in many respects been realized (3), but the phosphate concentrations of such solutions do not appear to be very closely correlated with the need for phosphate fertilization.

Failure to obtain such correlations for any ion originating in a relatively insoluble solid phase is explicable *if we recognize the fact* that the relation between soil and solution in the displacement process is that of a stable equilibrium

during the time covered by the displacement procedure; whereas the relation at the interphase between a solid particle of soil and an absorbing plant-root surface is constantly changing because of emanations by the roots and absorption by plants.

From these and other considerations, it seemed that a picture of the effect of a shifting equilibrium upon the phosphate released could best be developed by studying solutions obtained by displacement, *after the solution we call the "soil solution" is exhausted* (1). It was clear that such successive solutions should be increasingly diluted by the water used in the displacement procedure; that most constituents, including calcium, should decline in concentration, but because of

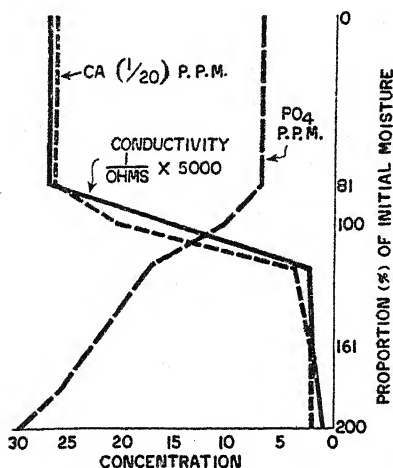


FIG. 2. RELATION BETWEEN TOTAL ELECTROLYTES—Ca AND PO<sub>4</sub>, DETERMINED BY DISPLACEMENT OF FRESNO FINE SANDY LOAM

Soil solution recovered 81 per cent. Further displacement (involving dilution) reveals inverse relation of Ca<sup>++</sup> and PO<sub>4</sub><sup>---</sup>.

this decline in calcium the concentration of phosphate should *increase*. These relations are found to hold when tested experimentally (see figure 2).

The striking inverse relation between phosphate and calcium solubilities evidenced in figure 2 brings out the very sensitive interdependence of these ions in the soil system. It is obvious that when the calcium concentration of soil solution of soils in place is reduced, as must happen during absorption by plants or after rains (or irrigation), there must be a concurrent increase of phosphate concentration in the liquid phase and a tendency to increase in the interphase at plant-root surfaces. As has been pointed out, this would be true from theoretical considerations alone, but the extent of the effect would hardly have been appreciated.

Changes of H<sup>+</sup> concentration are not a factor in this experiment, inasmuch as the successive solutions, though relatively uniform in pH, showed a progressive slight increase, which would tend to depress rather than increase phosphate solubility.

The extent of the effect of  $H^+$  on changes in calcium-phosphate systems, both as such and as modified by another solid phase calcium compound, is brought out in figure 3. The data are from mixtures of the various substances with the quantities of phosphate and calcium carbonate found in a particular soil, under intensive study in this laboratory at the time. It will be observed that the data, being expressed logarithmically, apparently minimize the effects on phosphate concentration, but afford easy comparison of rise of phosphate with changes of

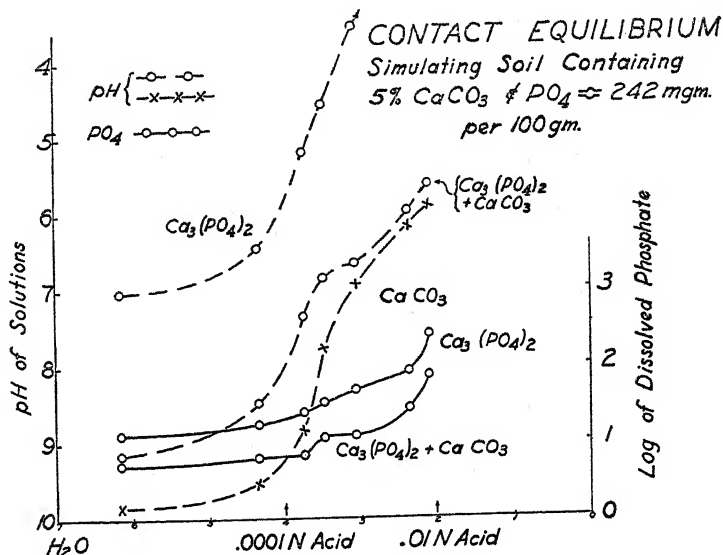


FIG. 3. EFFECT OF  $CaCO_3$  UPON SOLUBILITY OF  $Ca_3(PO_4)_2$  IN ACID

"Contact equilibrium" indicates a specific procedure and time of mixing in obtaining the solutions. This is described more particularly in the text. For present purposes it will suffice to say that the graphs would follow the same pattern if a longer period of mixing has been used, although the values would vary somewhat.

pH of the solutions—a point which will be stressed hereafter in data from soils (see figures 4 and 5).

#### LIMITATIONS OF EQUILIBRIUM STUDIES

It will be noted that in the preceding discussion, with the exception of the general reference to the significance of the very low figures for phosphate dissolved by acid from kaolinitic soils, no attempt was made to relate figures for solubility of phosphate in acid, directly to plant production or to the need of soil for phosphate fertilizer. Moreover, as suggested in a former paper (4), in which kaolinitic soils were discussed, it is the *type of behavior* shown by such soils which is instructive rather than the significance of any individual figure expressive of solubility. This is also true for the calcium-phosphate type of soils, but in these a general conformance to the type of behavior (fig. 1) is not so indicative as in the kaolinitic soils. This is unquestionably because the acid used to demonstrate the type of behavior induced secondary reactions in the *equilibrium* mixtures of



a mass of soil particles with a solution, which might not occur at an interphase where  $H^+$  may act on individual particles of the phosphate carrier.

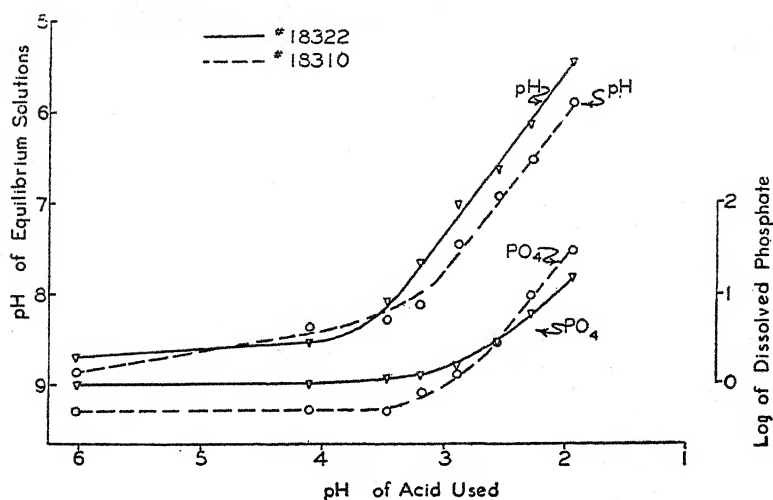


FIG. 4. EFFECT OF ACID UPON SOLUBILITY OF PHOSPHATE IN CALCAREOUS SOILS CONTAINING  $CaCO_3$

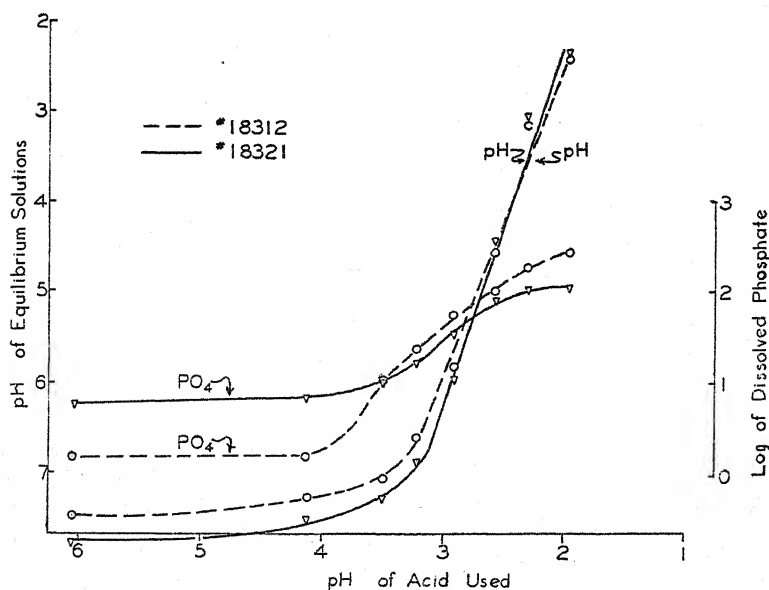


FIG. 5. EFFECT OF ACID UPON SOLUBILITY OF PHOSPHATE IN CALCAREOUS SOILS CONTAINING No  $CaCO_3$

Specifically, data obtained from *equilibrium* mixtures cannot show the relation between  $H^+$  acting on individual particles of phosphate carrier and the release

of phosphate to the solution because the  $H^+$  ion concentration *measured in the solution* is not the  $H^+$  *in play* but is that developed as a result of *all* reactions that have taken place. Moreover, the phosphate found in the *equilibrium* solution is not the phosphate released from the phosphate carrier, but is that which could be released diminished by a variable quota, the amount of which is also determined by secondary reactions which release ions, e.g.,  $Ca^{++}$ , capable of depressing phosphate solubility.

Equilibrium solutions with acids are, thus, analogous to soil solutions, inasmuch as they represent the resultant effect of *all* of the reactions brought about by changes in  $H^+$ . Hence, they do not give a true picture of the solubility of ions in the solid phase resulting from the  $H^+$  in the interphase between phosphate carrier and soil solutions or plant-root surfaces (5). It is the phosphate there released as the result of the continual emissions of acid by the plants, or reduction of calcium concentration, which has the best opportunity to enter the absorbing cells of the plant-root surfaces, and which, if determinable, might afford a rational basis for appraising the phosphate-supplying power of the soil.

It is not suggested that the phosphate thus released is *exactly* determinable or that, if determined, the figures would be capable of *narrow* interpretation in terms of the supplying power of the soil. It can, however, be demonstrated by experiment, that there are differences in solubility as *measured at equilibrium* from those obtained in *very brief* periods, and that with highly buffered soils the phosphate dissolved by acid is not only different but is actually *greater* as the time of contact of soil and reacting solution is *diminished*.

The technical difficulty in such experiments is so-to arrange the conditions that the time of contact of soil and solution will be *extremely* short, inasmuch as the mixtures tend to come to *substantial equilibrium* in extraordinarily short periods. We have attempted to surmount this difficulty by using larger ratios of solution to soil and filters of large surface.

#### CONTACT EQUILIBRIUM

When 2-gm. samples of air-dry soil is used to 100 cc. of HCl solutions (of any desired pH) in 100-cc. cylinders, inverted twice, and thrown on large folded filters, the time of contact, before filtration begins, is less than 10 seconds. Unfortunately, a further period of about 2 minutes is required until enough solution is collected for analysis<sup>3</sup>. This procedure, for convenient reference, is designated as "Contact Equilibrium" and, unless otherwise noted, was followed in obtaining all the data on the effects of acid presented hereafter.

It will be noted that the procedure is entirely arbitrary, is *not intended* to indicate the amount of  $PO_4$  ion in the soil solution, but is designed to reflect the extent to which phosphate would dissolve at an interphase, if and when the condition at such interphase is equivalent to the  $H^+$  concentrations developed in the solutions.

<sup>3</sup> By using tubulures packed with paper pulp and suction, the total elapsed time, including filtration, can be reduced to less than 10 seconds. The differences in dissolved phosphate by this technique do not, however, appear to be significant enough to warrant the trouble involved.

This procedure not only shortens time of contact but avoids handling of unnecessarily large volumes of solution. Data equivalent to titration, which reveal the type of behavior of a soil with eight solutions of varied pH, can be obtained in about an hour. Phosphate must, of course, be determined colorimetrically, as the amounts derived from 2-gm. samples are entirely too small for precipitation.

To illustrate the differences between phosphate dissolved by a given concentration of acid at substantial equilibrium as contrasted with that dissolved in minimum (applicable) time, data from four soils are presented in table 1.

The differences in the *amounts* of phosphate (3.2, 4.5) in the first two soils by the method which more nearly approximates the condition at plant-soil interphase seem entirely too small to account for the differences in fertilizer require-

TABLE 1

*Effect of time on solution of  $PO_4$  in calcium-dominated soils*

Reagent used, dilute HCl (pH 2.69); 2 gm. soil to 100 cc. of solvent

Elapsed time..	FINAL pH		MILLIGRAMS FOR 100 GM. SOIL DISSOLVED				SOLID PHASE	RESPONSE OF (OAT) PLANT TO PHOSPHATE FERTILIZERS
	E* 1 hr.	C† 130 sec.	Ca <sup>++</sup>		PO <sub>4</sub> <sup>---</sup>			
			E 1 hr.	C 130 sec.	E 1 hr	C 130 sec.		
18310	7.35	6.48	420	290	2.3	<3.2	CaCO <sub>3</sub> 6% CaSO <sub>4</sub> (large) CaCO <sub>3</sub> 5% CaSO <sub>4</sub> (some)	54 per cent increase.
18322	7.08	6.34	340	240	3.3	<4.5		No increase.
18312	6.17	4.64	380	380	108.0	>97.5		77 per cent increase.
18321	5.83	4.62	380	360	72.0	>65		1.5 per cent increase.

\* E = Substantial equilibrium. Other experiments indicate that longer contact does not increase dissolved phosphate substantially over that obtained in 1 hour of mixing on a rotor, as in this case.

† C = Contact equilibrium as previously described.

ment shown in the last column. Also, in the second pair of soils the amount of phosphate (97.5, 65) is actually greater in the soil having the greater need for phosphate fertilizer. Finally, the relatively great amounts of phosphate in the second pair as compared with the first pair are not consistently reflected in response of plants to fertilization.

The point of emphasis here is not that absolute or relative figures for phosphate can indicate supplying power to plants, but the *fact* that *in some soils more* phosphate may be accessible to plant-root surfaces (as exemplified in the shorter time of contact) than might be inferred from a study of equilibrium solutions or soil solutions.

In the first pair of soils the figures for pH and Ca<sup>++</sup> are both respectively lower for the shorter period and thus concur in explaining why the phosphates are higher than those found at equilibrium.

In the second pair of soils a similar comparison shows lower pH values for the shorter time of contact and equal or substantially equal calcium for both periods. Here, *despite* lower pH values, the phosphate is not higher, on short contact, but is *lower* in the absence of a markedly lower calcium content. The comparisons suggest that, if the time of contact could have been greatly shortened (say to  $\frac{1}{100}$  of a second) the trend shown in the first pair of soils might have been manifested to a greater degree, and the same trend might have appeared in the second pair. It is conceivable that figures obtained in extremely short periods might correlate with the known responses of the soil to phosphate fertilization. However that may be, the data demonstrate the difficulty of *avoiding* a condition approaching equilibrium. When we consider that most of the procedures for estimating the phosphate-supplying power of soils are deliberately predicated on techniques expressly designed to produce equilibrium conditions, we should not be surprised at the very general failure to give data reflecting differences in soils which are not shown equally well by comparisons of concentrations of displaced solutions or  $H_2O$  extracts (with minimal proportions of water), inasmuch as all such methods are alike in representing equilibrium conditions.

#### COMPARATIVE STUDY OF $H^+$ EFFECTS ON A GROUP OF 17 SOILS

Inferences from solubility studies as to the mechanisms by which phosphate ions are released from a solid phase of the soil may be entirely reasonable without being conclusive, because of our inability to reproduce the exact conditions existing at interphases between soil particles and root surfaces or between such particles and the soil solution. Quite apart, therefore, from any practical value of laboratory methods for predicting the need of a soil for phosphate fertilizer, it seems essential that such inferences be tested by comparison of the data with results obtained by growing plants in the particular soil.

Such comparisons were made on a group of soil samples previously studied to determine the percentage increase in yield of oat plants by a standard application of phosphate fertilizer.<sup>4</sup> The effects upon these soils of  $H_2O$  and of acid of various concentrations, at contact equilibrium, are shown in table 2.

The data presented are competent to show the effects upon phosphate solubilities which could occur in the respective soils, in place, if and *when* the pH values at soil-plant interphase were changed to those shown. What they fail to disclose is the extent to which typical plants could change the pH values or the calcium concentrations. Data from acid treatments and graphs obtainable therefrom are of interest, chiefly because they afford pictures of the relative resistance of individual soils to changes in pH which affect solubility of calcium and phosphate.

The data in table 2 indicate little relation between the results of acid treatments (below pH 4) and the measured response to phosphate fertilizer. On the other hand there *is*, with a single exception, a very striking relation between fertilizer need and comparatively "high" and comparatively "low" values for phosphate obtained with water alone (pH 6.07). With the exception noted

<sup>4</sup> Soils obtained through the courtesy of H. D. Chapman (7). Further information about these soils, unessential to our discussion, is given in Chapman's paper.

(18312)<sup>5</sup> all soils in which phosphate fertilizers gave substantial (i.e., more than 13 per cent) increases in yield gave less than 0.8 mgm. of phosphate per 100 gm. of soil by the procedure used. It would thus appear that, at least in highly buffered calcareous soils, the release of much less than 1 mgm. of phosphate per 100 gm. of soil at contact equilibrium is generally symptomatic of a need for phosphate fertilizer. In support and extension of this conclusion, Ayres, in this laboratory, has obtained highly corroborative results from some 200 additional

TABLE 2

*H<sup>+</sup> developed and phosphate dissolved by H<sub>2</sub>O and acid (HCl) from calcium-dominated soils, by contact equilibrium technique*

Ratio of liquid to soil, 50-1; PO<sub>4</sub> in mgm. per 100 gm. soil

CONCENTRATIONS OF ACIDS USED.....pH		6.07 (H <sub>2</sub> O)		4.12		3.64		3.29		2.91		2.57		2.28		1.96	
Soil number	Increase yields of oats due to phosphate fertilizer	pH	PO <sub>4</sub>	pH	PO <sub>4</sub>	pH	PO <sub>4</sub>	pH	PO <sub>4</sub>	pH	PO <sub>4</sub>	pH	PO <sub>4</sub>	pH	PO <sub>4</sub>	pH	PO <sub>4</sub>
	per cent																
18311	115	9.02	0.40	8.77	0.40	8.42	0.50	7.36	0.90	6.32	1.00	5.60	2.60	3.51	7.20	2.22	12.50
18320	114	9.42	0.45	9.16	0.45	8.92	0.55	8.12	0.60	7.35	1.06	6.93	1.92	6.24	4.60	6.08	11.85
18317	78	7.65	0.48	7.37	0.62	7.13	1.18	6.69	1.73	6.51	3.70	5.90	6.40	5.28	8.40	3.00	17.70
18312	77	7.48	1.50	7.27	1.50	7.08	10.40	6.58	23.40	5.84	53.50	4.59	96.00	3.16	183.00	2.44	263.00*
18316	69	6.60	0.36	6.35	0.36	6.11	0.36	5.85	1.30	3.61	1.60	2.93	1.80	2.41	2.40	2.01	2.70
18310	53	8.86	0.50	8.34	0.50	8.30	0.50	8.16	0.80	7.47	1.22	6.93	2.80	6.52	9.20	5.89	30.00†
18318	48	6.89	0.20	6.56	0.35	6.19	0.45	5.48	0.66	3.56	1.05	2.94	1.30	2.42	1.24	2.05	2.00
18315	13	6.65	0.80	6.43	0.80	6.16	1.60	5.52	2.60	3.81	4.20	3.06	6.50	2.53	13.20	2.11	16.70
18314	11	6.75	1.20	6.56	1.40	6.36	2.20	5.91	3.90	4.41	11.50	3.36	19.50	2.63	30.00	2.14	37.50
18319	3	6.95	1.08	6.61	1.14	6.35	1.40	5.63	2.00	3.76	3.70	3.19	5.65	2.65	6.50	2.30	15.00
18325	1.8	7.32	0.90	7.06	1.60	6.74	2.02	6.22	3.77	4.26	9.00	3.36	11.65	2.75	13.00	2.30	14.40
18324	1.6	7.22	1.27	6.90	1.44	6.48	2.00	6.00	3.40	3.89	6.80	3.17	8.50	2.58	10.70	2.20	11.00
18321	1.5	7.76	6.00	7.49	7.00	7.23	10.00	6.86	15.60	5.98	34.50	4.43	77.50	3.08	103.00	2.38	110.00*
18327	1.4	7.40	2.00	6.75	2.33	6.51	3.65	6.10	7.10	4.00	24.40	3.28	49.30	2.69	64.00	2.28	111.00
18313	0.0	6.80	1.70	6.39	1.80	6.18	3.90	5.56	5.60	3.73	10.9	2.98	14.30	2.45	21.00	2.05	32.30
18322	0.0	8.76	1.00	8.55	1.00	8.10	1.16	7.67	1.24	7.06	1.62	6.64	3.00	6.15	6.02	5.43	15.00†
18323	0.0	7.40	1.33	6.96	1.63	6.38	2.80	5.96	4.87	3.97	11.06	3.18	18.20	2.59	23.30	2.18	26.00

\* See figure 4.

† See figure 5.

soils which had been rated for phosphate fertilizer needs in pot cultures with several plant species.

From the point of view represented by this paper, however, any value attached to ability to make an enlightened guess as to the need of a soil for phosphate fertilizer, as a result of laboratory studies, is subordinate to the implication of the fact that extractions with a wide ratio of H<sub>2</sub>O to soil afford *more significant data* than those derived from extractions with minimal proportions of H<sub>2</sub>O or from so-called soil solution studies.

The implication referred to is that large proportions of water, by decreasing the *concentration* of calcium (and conversely increasing the solution of phosphate, cf. fig. 2) must *reflect* an analogous condition actually (and normally) existing at a plant-root surface, where the liquid phase is (in effect) being diluted in its calcium content by the more or less continuous uptake of that ion by the plant.

<sup>5</sup> The aberrant behavior of this soil is accounted for later in this paper.



It is difficult to conceive that the correlations demonstrated could have been shown if this were not the case. The fact that occasionally we find soils which respond to phosphate fertilizer giving comparatively high figures by extraction with a wide proportion of water to soil, as in soil 18312, does not vitiate the implications of the general relations shown, but merely indicates that, because of some peculiarity of the particular soil involved, the extreme degree of dilution imposed (in the extraction) causes a greater change in calcium concentration than that normally brought about by the plant in the field.

The high degree of correlation, shown in table 2, between relatively low figures and relatively high figures for phosphate, and between a need, or lack of need, for phosphate fertilizers, suggests that the acquisition of phosphate by plants is very largely conditioned by fluctuations of calcium in the soil-plant interphase, caused by the plants' own absorption of that ion.

In support of this theory is presented evidence obtained from this same group of soils by the method used in collecting the data presented in figure 2. This method is the displacement procedure (2) usual in studying the soil solution. It should be noted that by this procedure the *entire amount* of soil solution is never obtained. With sandy loam soils it is usually possible to recover 70-80 per cent of soil solution, that is, the conductivity of the solutions collected after that point falls, showing dilution by the displacing water. Thus the changed conductivity or "break" serves as a guide to separate soil solution from diluted solutions.

The successive solutions obtained after the "break" always diminish progressively, to a greater or less extent in calcium (and magnesium)<sup>6</sup> concentration, but the phosphate tends to increase, also to a greater or less extent, but differently in different soils. The increases or lack of progressive increases of phosphate shown by successive solutions in different soils thus reflect the capacity of each individual soil to release phosphate to solution if and when calcium is *somewhat* reduced. Similarly, if intake of calcium ions by a plant is greater than its intake of phosphate ions, as appears to be generally true when plants are grown on soil, it is in effect diluting the soil solution or interphase, with respect to calcium, just as we do in the laboratory by the procedure described.

In the experiments here discussed, to minimize work and time, the displacements were made on 50-gm. samples of air-dry soil. The small amounts of solution involved necessarily preclude separation and analysis of the small increments usual with large amounts of soil. No attempts were made to separate the solutions at the point represented by the "break," as it was obvious from former work that the effects could be shown even if the first solutions were slightly diluted. The increments of solution actually collected each represent 100 per cent of the water necessary to saturate the individual soils after being packed in the displacement tubes.

It will also be observed that the calcium content of the solutions was not quantitatively determined but is inferred from the decline in total concentration

<sup>6</sup> Magnesium is of course a factor, but quantitatively of less significance because of the more limited occurrence of this element in most soils.

(conductance), inasmuch as total concentration and calcium tend to decline in about the same degree (*cf.* fig. 2).<sup>7</sup>

Table 3 shows that the physiologically deficient soils, that is, those showing an increase of more than 13 per cent with phosphate fertilizer, *do not* increase measurably in phosphate in the second increment of solution displaced, and in only one instance is there an increase in the third increment. It also shows that the soils which are not physiologically deficient, as defined above, *all* increase measurably in the second increment.

Such a complete degree of correlation between the chemical behavior of these soils with the known responses of plants must be due to the fact that the trends shown by the laboratory data are directly related to the field responses of the plant used in the fertilizer test, even though the trends probably do not measure the field response exactly in individual cases. The correlation thus testifies to the dominant role of a fluctuating calcium concentration in the soil-plant interphase in releasing phosphate from a relatively insoluble solid phase and making it accessible to the absorptive influence of the plant.<sup>8</sup>

#### $H^+$ VERSUS $Ca^{++}$ AS FACTORS IN PHOSPHATE SOLUBILITY

Figures 4 and 5 present results of the effect of  $H_2O$  and acid upon the phosphate solubility of four soils (contact equilibrium extracts, 50-1, from table 2). For ease of reference it will be noted that the soils, in both figures, represented by dashes were physiologically deficient, as defined heretofore, and that the soils represented by solid lines did not require phosphate fertilizer.

It is at once evident that these data give little encouragement for predicting fertilizer needs. Although the physiologically deficient soils of each pair give lower figures for phosphate at all pH values possible in the soil-plant interphase, the phosphate in the physiologically deficient soil 18312, is much higher than that of soil 18322, containing  $CaCO_3$  but which does not require phosphate fertilizer.

The two figures do show characteristic differences between soils containing  $CaCO_3$  and those lacking in  $CaCO_3$ . In the former (fig. 4) the dissolved phosphate does not tend to increase substantially until the pH has been materially lowered. In the latter (fig. 5) the reverse is the case and the increase of phosphate precedes the decline in pH.

<sup>7</sup> Of course this is not invariably the case! For example, in soils containing large proportions of sodium salts and potentially soluble calcium, total concentration would decline to a greater degree than calcium. It will be observed later that we have not interpreted the results so narrowly that differences in individual soils in this respect would vitiate our conclusions.

<sup>8</sup> Although not essential to the present discussion, it will be noted that the 1-50 equilibrium extracts of the residual soil, after displacement, show considerable calcium and sulfate and that the soils which are physiologically deficient tend to have the largest amounts of these ions. There is little question but that many of the difficulties encountered in phosphate nutrition on soils of arid regions are caused by labile calcium derived from gypsum.

Though the latter type of behavior is, in general, a favorable sign, yet one of the soils manifesting it requires phosphate fertilization, and other examples showing a similar inconsistency could be given from this same group of soils.

In short, it appears impossible to integrate the results of such titrations with fertilizer requirements to a satisfactory degree. It certainly cannot be done with such soils as these, most of which contain more or less  $\text{CaSO}_4$  (see table 3). Nor does it seem likely that even in the absence of  $\text{CaSO}_4$  a high degree of correlation could be shown.

The fact is that  $\text{H}^+$ ,  $\text{Ca}^{++}$ , and  $\text{PO}_4^{---}$  comprise a mutually interdependent system in soils. The release of  $\text{H}^+$  at soil-plant interphase has little effect in lowering the pH of the system but a great effect in terms of dissolved calcium, which in turn depresses phosphate solubility. Moreover, the fluctuations in the relative concentration of calcium and phosphate in such interphases and in the soil solution are greatly affected by the relative absorption of those ions by

TABLE 3

*Displaced solutions and water extracts of soils known to respond substantially to phosphate fertilizers*

Test crop, oats. Conductance =  $\frac{1}{\text{ohms (res.)}} \times 10^5$ ; ( $\text{PO}_4$  in mgm. per liter of solution; mgm. per liter  $\times 5$  = mgm. per 100 gm. soil)

SOIL NUMBER.....	18311	18320	18317	13212	18316	18310	18318
Increased Yields with Phosphate Fertilizer ..... per cent	115	114	78	77	69	54	48
$\text{CaCO}_3$ in Soils.....	Heavy	Heavy	Heavy	Light	—	Heavy	—
1st Increment, Approximating Soil Solution, 100% of $\text{H}_2\text{O}$ at Saturation Capacity							
pH.....	7.8	7.8	7.67	7.60	7.15	7.12	7.27
Conductance.....	92.2	110.0	315.00	123.00	67.20	326.00	58.00
Relative Conductance.....	(100)	(100)	(100)	(100)	(100)	(100)	(100)
$\text{PO}_4$ .....	Nil	Nil	Nil	Nil	Nil	Nil	Nil
2nd Increment, 100% of $\text{H}_2\text{O}$ at Saturation Capacity							
pH.....	7.72	8.0	7.50	7.80	7.15	7.6	7.18
Conductance.....	37.10	50.9	253.00	37.90	17.50	257.0	16.00
Relative Conductance.....	(40)	(46)	(80)	(38)	(26)	(79)	(30)
$\text{PO}_4$ .....	Nil	Nil	Nil	Nil	Nil	Nil	Nil
3rd Increment, 100% of $\text{H}_2\text{O}$ at Saturation Capacity							
pH.....	8.0	8.13	7.55	7.90	7.00	7.48	6.95
Conductance.....	27.0	33.80	245.00	27.20	12.20	166.00	7.80
Relative Conductance.....	(29)	(30)	(78)	(22)	(18)	(50)	(14)
$\text{PO}_4$ .....	Nil	Nil	Nil	0.93	Nil	Nil	Nil
Equilibrium Water Extracts of Soils after Displacements (50 $\text{H}_2\text{O}$ -1 of Soil)							
Calcium.....mgm./l.	14.2	12.0	43.4	12.0	7.6	20.06	7.6
Sulfate.....mgm./l.	4.2	Nil	72.4	5.8	2.4	14.80	2.4
$\text{CaSO}_4$ equivalent to $\text{SO}_4$ mgm./100 gm.	30.0	Nil	5140	34.0	17.0	105.00	17.0

TABLE 3—Continued.

*Displaced solutions and water extracts of soils showing no substantial response to phosphate fertilizer*

SOIL NUMBER.....	18315	18314	18319	18325	18324	18321	18327	18313	18322	18333
Increased Yields with Phosphate.....per cent	13	11	3.1	1.8	1.6	1.5	1.4	0.0	0.0	0.0
CaCO <sub>3</sub> in Soil.....	—	—	—	—	—	—	—	—	Heavy	—
1st Increment, Approximating Soil Solu., 100% of H <sub>2</sub> O at Saturation Capacity										
pH.....	7.25	7.45	7.35	7.4	7.7	7.92	7.3	7.50	7.65	7.75
Conductance.....	58.50	72.70	50.30	62.5	90.6	98.50	48.3	49.30	446.00	89.90
Relative Conductance.....	(100)	(100)	(100)	(100)	(100)	(100)	(100)	(100)	(100)	(100)
PO <sub>4</sub> .....	Nil	Nil	Nil	Nil	Nil	4.75	2.1	1.32	Nil	Nil
2nd Increment, 100% of H <sub>2</sub> O at Saturation Capacity										
pH.....	7.18	7.45	7.27	7.6	7.9	7.80	7.4	7.67	7.95	7.94
Conductance.....	20.70	21.50	14.70	22.5	31.8	29.40	14.5	25.40	98.50	32.70
Relative Conductance.....	(35)	(30)	(29)	(36)	(35)	(30)	(30)	(51)	(22)	(36)
PO <sub>4</sub> .....	0.53	0.78	1.11	1.5	1.5	10.25	7.5	2.40	0.70	1.26
3rd Increment 100% of H <sub>2</sub> O at Saturation Capacity										
pH.....	7.20	7.63	6.90	7.9	7.8	8.20	7.4	7.9	8.16	7.95
Conductance.....	10.90	13.00	7.20	12.6	16.5	29.40	9.1	16.5	47.10	18.20
Relative Conductance.....	(18)	(18)	(13)	(20)	(18)	(30)	(19)	(33)	(11)	(20)
PO <sub>4</sub> .....	1.04	0.96	1.10	3.0	3.4	10.05	13.6	3.6	0.97	1.72
Equilibrium Water Extracts of Soils After Displacement (50 H <sub>2</sub> O-1 of soil)										
Calcium.....mgm./l.	7.6	7.6	8.6	Lost	7.6	13.0	6.6	6.6	13.0	4.4
Sulfate.....mgm./l.	4.2	4.2	Nil	0.8	2.4	4.2	0.8	4.2	6.2	2.4
CaSO <sub>4</sub> equivalent to SO <sub>4</sub> mgm./100 gm.	30	30	Nil	6	17	30	6	30	44	17

the plant. All of the available data indicate that the intake of calcium by plants growing in soils is quantitatively greater than their intake of phosphate, even though culture solution experiments indicate that phosphate absorption is more rapid than that of calcium from single salt systems.<sup>9</sup> When the intake of calcium and phosphate by growing plants in soils is expressed in terms of equivalents (ions), the discrepancy is even greater. The plant is thus continually shifting the equilibrium in the direction favorable to the solution of phosphate. It is not the amount of calcium taken up by the plant which determines the release of phosphate from soil particles, but the degree to which given plants shift the equilibrium in the liquid phase as a result of absorption of more calcium than phosphate.

It should be noted that although it appears, in general, that plants *tend* to shift the equilibrium of soil solution or interphase, the nature of the soil deter-

<sup>9</sup> The reason why plants growing in soils generally absorb more calcium than phosphate is, of course, that the calcium concentrations tend to be much higher than those of phosphate in the liquid phase of most soils.

mines whether that tendency will be translated into an *actual* shift great enough to account for solution of phosphate at a rate adequate for the requirements of the plants. For example, our own experiments suggest that in soils containing much gypsum the plant has great difficulty in depressing calcium concentration enough to enhance the solution of phosphate to the degree necessary to its requirement. Thus (cf. table 3) the three soils which contain the most solid-phase  $\text{CaSO}_4$ , 18317, 18310, and 18322, all show relatively high salt concentrations (conductances) in the first increment of displaced solution. In the first two soils, continued displacement reduces the conductance very slightly, and there is no measurable increase in phosphate. In the third soil the successive increments decrease greatly in conductance, and phosphate increases accordingly. The conclusion seems obvious that their differences in phosphate fertilizer requirement are due to the fact that calcium ion can be sufficiently reduced by plants to ensure adequate phosphate supply from soil 18322 and cannot in the other two soils. The reason for this can be assigned to the larger amounts of  $\text{CaSO}_4$  in the latter soils. In other soils the same effect might be caused by differences in the size of the particles of  $\text{CaSO}_4$  source materials, which determine the rate at which calcium is released to the liquid phase in partial or complete replacement of that withdrawn by the plant.

#### PHOSPHATE IN SOILS OF ORGANIC ORIGIN (PEATS)

Because of the solubility of organic matter in the usual reagents, determination of the sources of phosphate ion in soils of organic origin presents technical difficulties not encountered in mineral soils. Such dissolved organic matter must be oxidized to permit phosphate determination in the solutions, and there is always a question as to whether the phosphate found is derived from phosphate ion in the solution or from oxidation of phosphorus in some undetermined organic complex.

In soil solutions, water and acid extracts, the amounts of organic matter dissolved are small and are generally believed to be largely carbohydrate in nature, rather than proteinaceous, and any large amount of contamination of phosphate ion by that derived from oxidation of organic phosphorus seems inherently improbable.

Alkaline extracts or solutions, however, contain substantial amounts of organic matter, both in true solution and dispersed as sols, which cannot be separated by filtration or even by centrifuging. One is always in doubt as to whether the determined phosphate is due to oxidation of phosphorus-carrying organic compounds, to adsorbed phosphate, or to phosphate ion as such. It is true that much of the organic matter in alkaline solutions may be separated by centrifuging, after acidulating with fairly concentrated acid, but here there is another source of error, in that the acidulation produces the condition (low pH) favorable to the adsorption of phosphate ion by the organic matter thus separated and may thus lower the amount of phosphate subsequently determined in the solution phase.

Despite these technical difficulties which sometimes require qualification in



interpretation of data from peat soils, their main points of difference from mineral soils, with respect to phosphate, are easily established, even though different kinds of peat may be expected to vary.

A "fen" type of peat of extensive occurrence in the delta of the San Joaquin and Sacramento Rivers of California has supplied the material for most of our experiments.

Its more obvious characteristics are indicated by the comparison, in table 4, of its soil solution with those of mineral soils and with another type of peat from Minnesota.

The point of interest to the present discussion is the low concentration of phosphate ion. This is, of course, accounted for by the high concentration of

TABLE 4  
*Composition of soil solutions*

	MEAN OF 7 MINERAL SOILS	CALIFORNIA PEAT (TYPHA AND SCIRPA)	MINNESOTA (SPHAGNUM)
	<i>mgm./l.</i>	<i>mgm./l.</i>	<i>mgm./l.</i>
NO <sub>3</sub> .....	1043.0	2004.00	1305.0
HCO <sub>3</sub> .....	73.0	60.00	....
Cl.....	263.0	1870.00	389.0
SO <sub>4</sub> .....	238.0	2902.00	....
PO <sub>4</sub> .....	5.4	0.86	....
SiO <sub>2</sub> .....	47.9	n.d.	....
Ca.....	381.0	980.00	534.0
Mg.....	107.0	650.00	216.0
Na.....	116.0	1240.00	....
K.....	75.0	36.00	63.0
Total.....	2349.0	9751.00	....
pH.....	7.0	5.6	....
H <sub>2</sub> O content (moist basis) ..... <i>per cent</i>	16.2	59.7	65

calcium and magnesium characteristic of the solution. The following tabulation from our tank experiments reflects the depressing influence of these latter ions upon soluble phosphate. Fertilizer (CaH<sub>2</sub>PO<sub>4</sub>)<sub>2</sub>, was applied to plots of soil in amounts equivalent to 1,000 pounds per acre.

Dates.....	5/25	6/14	6/30	7/20	8/3	9/2
PO <sub>4</sub> in soil solutions (mgm. per liter)						
Unfertilized check.....	0.86	1.14	1.2	1.04	1.04	0.7
Fertilized (potatoes).....	2.46	3.06	2.4*	2.2*	1.5*	1.3*

\* At these stages the effect of the crop of potatoes could be partly responsible for lower phosphate.

The dominant influence of high calcium (and magnesium) is here obvious in the resulting low phosphate figures, inasmuch as Ca(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub> readily dissolves to

give 2 moles  $\text{H}_2\text{PO}_4$  for each 3 moles of fertilizer. If hydrolysis had not been inhibited the soil solution should have contained 300 or 400 mgm.  $\text{PO}_4$  per liter in the fertilized soil. Because of the inhibiting effect of calcium and magnesium, it is impossible materially to enhance the phosphate concentration of the soil solution of such soils by fertilization.

Unless contaminated with mineral sediments, such soils should contain no substantial quantity of calcium phosphate. That this is so is shown by analysis of samples, before and after leaching with enough 0.1 N HCl to remove all of the calcium phosphate, when the water-free soil has been found to contain phosphate, 358 mgm. per 100 gm. before leaching and 329 mgm. per 100 gm. after leaching; by difference, 29 mgm. per 100 gm. of phosphate ion from inorganic sources.

Moreover, when displaced in a manner similar to that used in table 3, the phosphate in the displaced solutions *does not* increase significantly in successive increments as it usually does (in the absence of  $\text{CaSO}_4$ ) in all mineral soils of the calcium phosphate type.

An experiment gave the following results:

- 1st 100% Displacement—Conductivity 28.1;  $\text{PO}_4$  3.1 mgm. per liter
- 2nd 100% Displacement—Conductivity 17.8;  $\text{PO}_4$  3.8 mgm. per liter
- 3rd 100% Displacement—Conductivity 14.0;  $\text{PO}_4$  3.6 mgm. per liter

This experiment was performed on a sample which had been leached with water to free it from water-soluble calcium and kept in the air-dry condition until displaced.

The first increment of solution is, therefore, not a true soil solution in the sense in which that term is ordinarily used, that is, a solution produced as a result of biological activity, but is merely the result of solution processes.

The successive increments of solution collected in this experiment cannot increase substantially in phosphate content, because even though the conductivities decline somewhat, the absolute values for this factor are so small that the concurrent changes in calcium must be too slight to affect materially the equilibrium between liquid phase and inorganic phosphate.

The significant comparison would appear to be between the phosphate concentration of the true soil solution (1- mgm. per liter) and that of the first increment of solution (3+ mgm. per liter) in the experiment. This increase, however, is a result of the removal of *all soil solution calcium*, which was brought about by leaching with amounts of water equivalent to many thousand per cent of the displaced solution. This treatment is not comparable to the treatments of mineral soils previously discussed where the comparisons which appear to have significance were between the soil solution (1st increment, 100% of soil solution) and the solution obtained immediately thereafter (second increment, 100% of soil solution).

We conclude that in peat soils any shift in the equilibrium in the soil solution or soil-plant interphase, caused by unequal absorption of calcium and phosphorus by the plants, could have little influence on the solubility of the small amount of inorganic phosphate these soils normally contain.

The data given above suggest that the small content of inorganic phosphate present is of secondary origin, phosphate escaping from the organic phase being precipitated *in situ* by the high concentrations of calcium and magnesium characteristic of these soils.

We have determined the adsorption capacity of this soil by the usual method of mixing soil with 10 times its weight of 0.025 *M*  $\text{KH}_2\text{PO}_4$ . After such treatment, the excess of reagent must, of course, be removed. We have attempted to do so by the displacement procedure using amounts of water equivalent to three times the water-holding capacity of the sample. Later, however, it was found upon extracting the residual soil with water that phosphate was liberated copiously and it was impossible to tell whether such phosphate was derived from hydrolysis of adsorbed phosphate or merely represented a little of the occluded residue of the very concentrated  $\text{KH}_2\text{PO}_4$  solution used in the attempt to saturate.

The results to date are inconclusive, but they suggest that either the organic matter does not adsorb phosphate, in the usual sense of the term, or if it does, holds it by such weak linkages that it should be readily released to the soil solution or plant. This is noteworthy as contrary to the behavior of mineral soils and has important implications in fertilizing soils primarily organic.

The following general conclusions are drawn from the experiments with peat soil:

The phosphorus content of these soils is largely in various forms of combination with organic matter, depending upon the kind of plant material from which the soils are derived and the stage of decomposition which they have attained. From the point of view of its ultimate utilization by growing plants, the phosphorus may exist in the following three conditions:

1. Phosphorylated carbohydrates.
2. Esters of the type of phytin known to occur in substantial quantity in many plants (8).
3. Protein phosphorus.

The first class could possibly be absorbed directly by growing plants, but the amounts would probably be small. Such complexes are so unstable, so easily hydrolyzable by enzyme action, that their existence in soil would probably be very transitory.

The second class could be the source of phosphate ion, to the extent the ions are present as a result of progressive hydrolysis by enzyme action.

The third class is probably the main source of phosphate ion to the soil system as a result of progressive oxidation of the protein complexes. Since such complexes are relatively stable, their release of phosphate would be fairly slow and would depend upon the intensity of biological oxidation in each soil.

Phosphate ion thus released could be directly absorbed by plants at the moment of liberation but if not absorbed would be immediately immobilized as calcium phosphate owing to the high concentration of calcium in the soil solution. In any event, the chemical criteria suggested heretofore for appraising supplying power of mineral soils are not generally applicable to peat soils strictly so called. There is an exception to this in that peat soils which contain in their soil solutions more than the amounts of phosphate found necessary in culture solutions (2-3 mgm. per liter) probably will not require phosphate fertilization for most plants.

#### SUMMARY

The natural result of the very general occurrence of potentially soluble calcium compounds in mineral soils, and the relatively low solubility of compounds

of that element with phosphate, is that some form of calcium-phosphate is the primary source material for phosphate in soil systems.

From the data at hand, it is highly probable that most of these phosphate complexes are of secondary origin and of variable proportions of calcium to phosphate, depending upon conditions at the time of formation. Whether of primary or secondary origin, the relatively insoluble phosphates are mineral aggregates rather than molecular species. As such, solution of phosphate ion occurs at the surface, and the rate of solution is largely determined by the extent of surface, unless the solvent is of such a nature and intensity as to break down completely the structural units of the mineral in question.

Phosphate ions escaping from such minerals or resulting from oxidation of organic phosphorus can be adsorbed by certain types of clay minerals (kaolinitic types) or by hydrated oxides of iron and alumina, under certain conditions. Such adsorbed phosphate is not readily released to soil solution or plant under the normal conditions existing at soil-plant or soil-soil-solution interphase.

The classification of the phosphate carrier of soils into one or the other of these types is desirable and can be accomplished by studying the relation of dissolved phosphate to changes in pH in mixtures of soil with dilute acid,  $H_2O$ , and alkali.

The extent to which phosphate comes into solution when the concentration of calcium in the soil solution is somewhat lowered can be demonstrated by comparing the phosphate concentrations of successive increments of displaced solutions. The effect of  $H^+$  released by plant action upon the phosphate carrier in a soil cannot be measured *in vitro* because the acid acts upon other soil constituents which release calcium ion and depress phosphate solubility. The same objection holds for use of any solvent applied to the entire soil at equilibrium, inasmuch as the effect of the solvent upon the phosphate carrier cannot be isolated from the secondary effects upon the nonphosphate-calcium carriers of the soil. If the time of contact between soil and solvent is shortened to the least that is practicable, it can be demonstrated that more phosphate is released from some soils, under these conditions, than is freed at equilibrium. When this is the case it demonstrates that at least some of the secondary reactions, inescapable in equilibrium studies, have been eliminated. The data may thus reflect more nearly what would happen in the soil-plant interphase where the solvent ( $H^+$ ) could act directly on the phosphate carrier.

When a considerable group of soils, the phosphate requirement of which had been demonstrated in pot experiments with oat plants, was studied by making water and acid extracts *with large proportions of solvent to soil*, little relation could be demonstrated between their fertilizer requirements and extractable phosphate when more than minimal amounts of  $H^+$  were involved, but the water extracts showed a high degree of correlation. This result confirms the earlier conclusion that the concentrations of calcium in the soil solution are the dominant influence in determining phosphate concentrations in the liquid phase of the soil.

When the same soils were displaced, the second increment of solutions obtained never gave substantial increases in phosphate concentration over the first in-

crement, in the physiologically deficient soils, whereas the physiologically adequate soils always showed such increases.

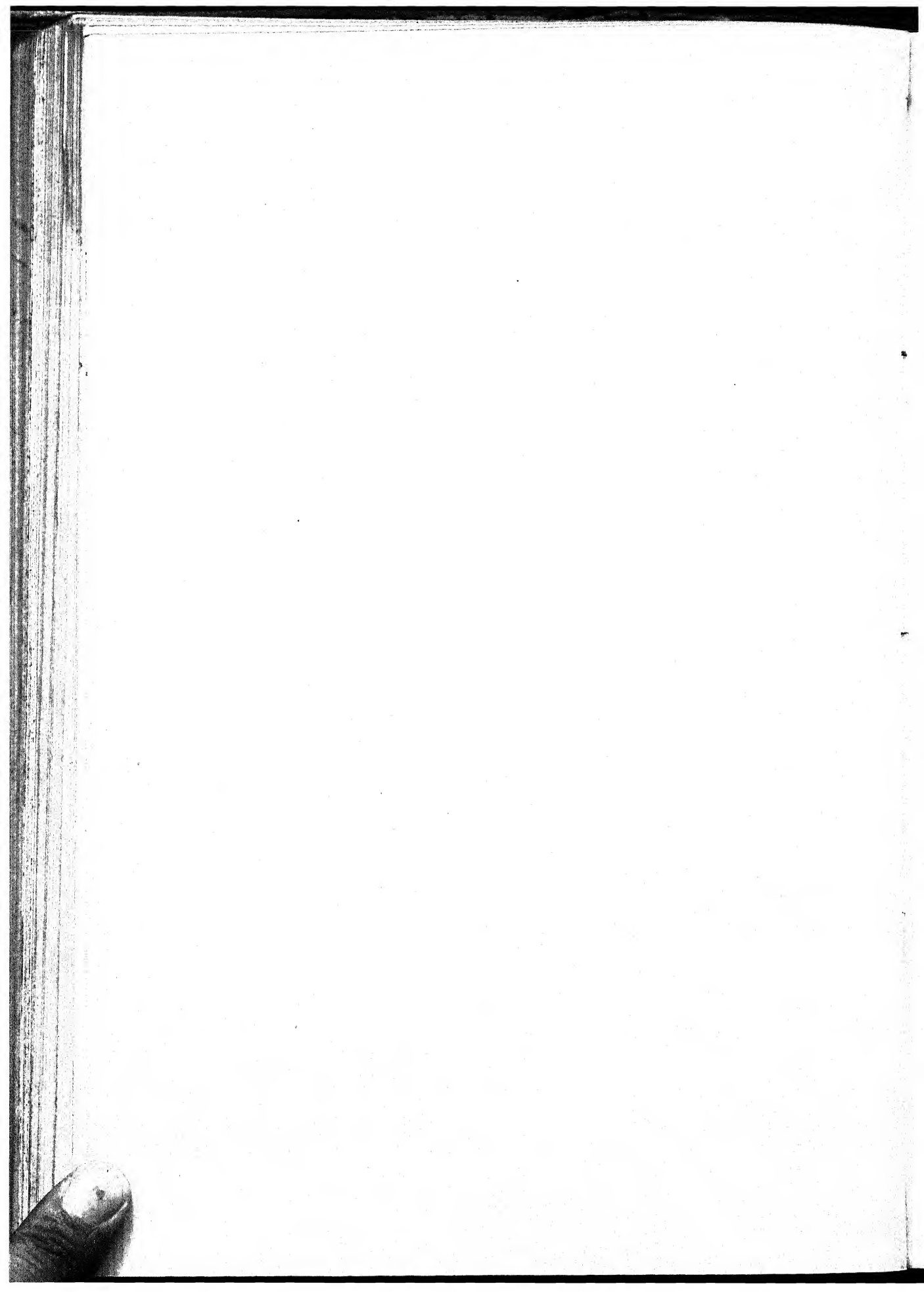
Whether the concentration of calcium is diminished by using a wide ratio of water in water extracts, or by the leaching involved in displacement, the lowered calcium concentration tends to be reflected in higher phosphate concentrations and there seems to be a fairly consistent relation between the results obtained by either means and what the plant can do when grown in the individual soils. This must mean that the acquisition of phosphate by a plant from a soil, in which the phosphate component is relatively insoluble, is largely determined by the extent to which the plant itself shifts the equilibrium between calcium and phosphate in the soil solution or in the plant-soil interphase.

The influence of such plant-induced shifts in the equilibrium would appear to be a minor factor in soils which are primarily organic. First, such soils contain relatively little inorganic phosphate; and second, the very high concentrations of calcium, and magnesium, in their soil solutions would preclude a very great change in the ratio of these ions to dissolved phosphate as a result of plant action.

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## SODIUM CONTENT OF SOME NEW JERSEY PLANTS<sup>1</sup>

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The Na content of the lithosphere, as given by Clark,<sup>2</sup> is 2.75 per cent. The K content is estimated at 2.58 per cent. The hydrosphere contains an estimated 1.14 per cent Na and only 0.04 per cent K. Despite the higher percentage of Na than K in terrestrial matter, plants generally contain much less Na than K.<sup>3</sup>

Although plants usually contain appreciable amounts of Na, there is, as yet, no certainty that this element has any specific nutritional function in them. Some plants, notably certain cultivated members of the Chenopodiaceae and Cruciferae and some wild species of Plantago, Iva, Spartina, and Salsola, contain fairly large amounts of Na. Nevertheless, relatively little attention has been paid to Na as a factor in plant growth.

There is some justification for neglecting the study of Na in plants, since the standard methods of analyses employed for determining this element have not been nearly so dependable as those for the other basic cations. The recent development of flame-photometer technique completely overcomes this difficulty. The procedure is rapid and gives reproducible results, even for small concentrations of Na.

This paper presents the results of a survey of the Na content of important native and cultivated plants of New Jersey. The survey was initiated with the specific purpose of locating, for use in an intensive study of the possible value of Na as a fertilizer constituent, plants that tend to accumulate this element. To this end, over 300 plant samples have been examined.

### EXPERIMENTAL METHODS

Native and cultivated plants of both the Appalachian and Coastal Plain soil provinces of New Jersey were collected, oven-dried at 80° C., ground in a Wiley mill, and analyzed for their Na content by the use of a Model-18, Perkin-Elmer, flame photometer. A colorless solution of the plant material was obtained by wet digestion of 0.5 gm. of dry tissue with HNO<sub>3</sub> and HClO<sub>4</sub>. When digestion was completed, the precipitated SiO<sub>2</sub> was filtered off, the acidity of the solution was adjusted to 0.02 N with HCl, the solution was made up to the proper volume with distilled water, and a portion of it was employed in the photometer. Each of the recorded values of Na represents the average of three readings. Since the

<sup>1</sup> Journal Series paper of the New Jersey Agricultural Experiment Station, Rutgers University, department of soils.

<sup>2</sup> Clark, F. W. The data of geochemistry, ed. 5. U. S. Geol. Survey Bul. 770. 1924.

<sup>3</sup> Beeson, K. C. The mineral composition of crops with particular reference to the soils in which they were grown. U. S. Dept. Agr. Misc. Pub. 369. 1941.

K content of the samples could be determined readily and quickly from the same solution, the content of this element was also recorded.

#### RESULTS AND DISCUSSION

The results of the general survey are presented in tables 1, 2, 3, and 5. The Na and K values are listed as minimum, maximum, and average values. Data on single samples for any one plant are listed under the average values. The grouping of the plants is quite arbitrary, but no better arrangement could be agreed upon.

The data show tremendous variations in both the Na and K contents of the various plants. In general, the Na content of the plants examined was very low in comparison with their K content. Certain species of *Typha*, *Siegingia*, *Iva*, *Spartina*, and *Salsola* found in salt-marsh and dune areas were exceptions, some of these being higher in Na than in K.

Of the 15 grasses examined, only four had a Na content exceeding 0.10 per cent. These latter plants, species of *Festuca*, *Siegingia*, *Spartina*, and *Sporobolus*, are normal inhabitants of either salt-marsh or dune areas. Species of *Poa*, *Bromus*, *Avena*, *Dactylis*, *Agrostis*, *Secale*, *Phleum*, and *Triticum* that were examined had an average Na content of only 0.04 per cent. A greater range was found in the Na content of plants native to salt-marsh areas than of those growing on normal soils. For example, the minimum and maximum percentages of Na in broom grass were 0.04 and 0.23, respectively, whereas the range in oats was only between 0.04 and 0.10 per cent. Rye and wheat exhibited an even smaller variation than oats. With the exception of those that are native to salt-marsh areas, and the further possible exception of oats, none of the grasses showed any tendency to accumulate Na.

The sedge group of plants, members of two genera of which were examined, were found to be Na accumulators. This is to be expected, since these plants are normal inhabitants of salt-marsh areas. *Carex* showed a range of Na values between 0.03 and 1.49 per cent.

Of the 11 legumes analyzed, only Ladino clover, red clover, and wild white clover gave any indication of Na accumulation. Alfalfa, by reason of its origin, might be expected to be high in Na, but it contained less of the element than the clovers. The Na content of the legumes, without the addition of Na to the substrate, tended to be a little higher than that of the grasses.

Of the 15 deciduous trees, the leaves of which were examined, not one exhibited any indication of being a Na accumulator. The range in Na content listed in table 1 was small, and the average was 0.04 per cent. The three species of oak were especially constant in their content of Na. The samples of black oak were collected from soils of widely different total Na content.

None of the three coniferous trees, juniper, pine, and red cedar, was found to be a Na accumulator. The Na content was quite similar to that of the deciduous trees.

Of the 16 species of common weeds examined, some belonged to the group of Na accumulators and some did not. Certain species of *Xanthium*, *Neslia*, *Plan-*

TABLE 1  
Na and K\* contents of some native and cultivated New Jersey plants  
Dry weight basis

COMMON NAME	SCIENTIFIC NAME	Na			K			SAM- PLES ANA- LYZED	TYPE
		Mini- mum	Maxi- mum	Aver- age	Mini- mum	Maxi- mum	Aver- age		
		%	%	%	%	%	%		
Grasses—complete tops									
Bluegrass.....	<i>Poa pratensis</i>	....	....	0.00	....	....	1.03	1	I
Broom grass.....	<i>Festuca elatior</i>	0.04	0.23	0.13	0.65	0.75	0.70	2	II
Brome grass.....	<i>Bromus</i> sp.	....	....	0.05	....	....	2.65	1	I
Crabgrass.....	<i>Syntherisma san- guinalis</i>	....	....	0.04	....	....	2.94	1	I
Dune grass.....	<i>Sieglingia pur- purea</i>	....	....	0.37	....	....	0.92	1	IV
Oats.....	<i>Avena sativa</i>	0.04	0.10	0.07	1.03	1.04	1.03	2	II
Orchard grass.....	<i>Dactylis glomerata</i>	0.04	0.04	0.04	1.10	1.18	1.14	2	I
Redtop.....	<i>Agrostis alba</i>	....	....	0.04	....	....	1.57	1	I
Rye.....	<i>Secale cereale</i>	0.02	0.04	0.03	0.55	1.65	1.10	2	I
Salt meadow grass...	<i>Spartina patens</i>	0.32	0.48	0.39	0.23	0.36	0.31	3	IV
Slender wheat grass.	<i>Agropyron tenerum</i>	0.04	0.08	0.06	0.65	1.85	1.20	2	I
Timothy.....	<i>Phleum pratense</i>	0.03	0.06	0.04	0.98	2.98	2.01	3	I
Wheat.....	<i>Triticum vulgare</i>	0.03	0.03	0.03	1.04	1.73	1.38	3	I
Wheat-straw.....	....	....	....	0.00	....	....	0.13	1	
Wire grass.....	<i>Sporobolus</i> sp.	....	....	0.13	....	....	1.03	1	IV
Sedges—complete tops									
Sedge.....	<i>Scleria verticillata</i>	....	....	0.38	....	....	0.52	1	IV
Sedge.....	<i>Carex</i> spp.	0.03	1.49	0.34	0.63	1.20	0.85	5	II or IV
Legumes—complete tops									
Alfalfa.....	<i>Medicago sativa</i>	0.01	0.10	0.05	0.75	2.80	1.70	30	I
Birdsfoot-trefoil....	<i>Lotus corniculatus</i>	....	....	0.01	....	....	1.78	1	I
Ladino clover.....	<i>Trifolium repens</i> var. <i>latum</i>	0.07	0.25	0.16	1.12	2.60	1.82	22	II
Lespedeza.....	<i>Lespedeza sericea</i>	....	....	0.03	....	....	0.65	1	I
Red clover.....	<i>Trifolium pratense</i>	0.02	0.24	0.07	0.85	2.12	1.64	9	II
Sweet clover..	<i>Melilotus alba</i>	0.03	0.06	0.04	0.91	2.60	1.78	6	I
	<i>Melilotus officinalis</i>	....	....	0.08	....	....	0.95	1	I
White clover.....	<i>Trifolium repens</i>	....	....	0.11	....	....	1.80	1	II
Vetch.....	<i>Vicia cracca</i>	0.04	0.08	0.06	0.96	2.55	1.49	3	I
Hairy vetch.....	<i>Vicia hirsuta</i>	....	....	0.02	....	....	2.47	1	I
Soybeans.....	<i>Soja max</i>	....	....	0.03	....	....	1.55	1	I
Trees (deciduous)—leaves only									
Ash, white.....	<i>Fraxinus Amer- icana</i>	....	....	0.06	....	....	0.83	1	I
Birch, white.....	<i>Betula populifolia</i>	0.03	0.05	0.04	0.94	1.11	1.02	2	I

\* Because of the close relationship between Na and K, both elements are reported.

TABLE 1—Continued

COMMON NAME	SCIENTIFIC NAME	Na			K			SAM- PLES ANA- LYZED	TYPE
		Mini- mum	Maxi- mum	Aver- age	Mini- mum	Maxi- mum	Aver- age		
		%	%	%	%	%	%		
Trees (deciduous)—leaves only—Continued									
Catalpa.....	<i>Catalpa Catalpa</i>	....	....	0.04	....	....	1.67	1	I
Cherry, wild.....	<i>Prunus Virginiana</i>	0.03	0.06	0.04	0.93	1.13	1.03	2	I
Chestnut.....	<i>Castanea dentata</i>	....	....	0.02	....	....	0.85	1	I
Dogwood.....	<i>Cornus florida</i>	0.02	0.07	0.04	0.75	1.25	0.94	3	I
Hickory.....	<i>Hicoria ovata</i>	....	....	0.04	....	....	0.70	1	I
Maple, red.....	<i>Acer rubrum</i>	....	....	0.10	....	....	0.83	1	I
Maple, silver.....	<i>Acer saccharinum</i>	0.04	0.05	0.04	0.97	1.30	1.13	2	I
Mulberry.....	<i>Broussonetia papy- rifera</i>	....	....	0.10	....	....	1.56	1	I
Oak, black.....	<i>Quercus velutina</i>	0.03	0.04	0.03	0.77	0.95	0.85	3	I
Oak, post.....	<i>Quercus lyrata</i>	0.01	0.04	0.02	0.53	0.53	0.53	2	I
Oak, white.....	<i>Quercus alba</i>	....	....	0.04	....	....	0.53	1	I
Sassafras.....	<i>Sassafras Sassa- fras</i>	....	....	0.01	....	....	0.97	1	I
Tree-of-Heaven....	<i>Ailanthus glandu- losa</i>	....	....	0.02	....	....	1.93	1	I
Trees (conifers)—leaves only									
Juniper.....	<i>Juniperus commu- nis</i>	....	....	0.05	....	....	0.20	1	I
Pine.....	<i>Pinus Virginiana</i>	0.01	0.06	0.04	0.36	0.63	0.48	3	I
Red cedar.....	<i>Juniperus Virgin- iana</i>	0.02	0.04	0.03	0.33	0.65	0.52	3	I
Common weeds—complete tops									
Bindweed.....	<i>Ipomoea lacunosa</i>	....	....	0.05	....	....	2.42	1	I
Burdock.....	<i>Xanthium stru- marium</i>	0.03	0.21	0.12	4.20	5.75	4.97	2	II
Carrot, wild.....	<i>Daucus Carota</i>	0.00	0.06	0.03	2.50	3.35	2.99	5	I
Dandelion.....	<i>Taraxacum Tarax- acum</i>	....	....	0.04	....	....	4.00	1	I
Dock.....	<i>Rumex crispus</i>	0.03	0.06	0.04	2.50	4.75	3.62	2	I
Milkweed.....	<i>Asclepias rubra</i>	0.00	0.03	0.02	2.18	2.58	2.38	2	I
Lambs quarters....	<i>Chenopodium al- bum</i>	....	....	0.00	....	....	4.32	1	I
Mustard.....	<i>Neslia paniculata</i>	0.01	0.34	0.06	1.22	2.88	2.07	12	II
Plantain, common...	<i>Plantago major</i>	0.02	0.09	0.05	2.50	3.80	3.01	3	II
Plantain, narrow....	<i>Plantago lanceolata</i>	0.00	0.47	0.14	0.95	2.22	1.53	5	II
Plantain, Rugels....	<i>Plantago Rugelii</i>	....	....	0.04	....	....	2.30	1	II
Ragweed.....	<i>Ambrosia trifida</i>	....	....	0.02	....	....	2.13	1	I
Shepards purse.....	<i>Bursa Bursa- pastoris</i>	....	....	0.02	....	....	1.13	1	I
Sorrel.....	<i>Rumex Acetosella</i>	....	....	0.52	....	....	1.55	1	III
Thistle, Russian....	<i>Salsola Tragus</i>	....	....	0.01	....	....	3.06	1	I
Yarrow.....	<i>Achillea Mille- folium</i>	0.00	0.22	0.10	0.90	4.49	2.15	5	II



TABLE 1—*Concluded*

COMMON NAME	SCIENTIFIC NAME	Na			K			SAM- PLES ANA- LYZED	TYPE
		Mini- mum	Maxi- mum	Aver- age	Mini- mum	Maxi- mum	Aver- age		
		%	%	%	%	%	%		
Berries—leaves only									
Blackberry.....	<i>Rubus villosus</i>	0.03	0.07	0.05	0.27	1.73	1.00	4	I
Cranberry.....	<i>Oxycoccus Oxycoc- cus</i>	0.00	0.03	0.01	0.47	0.70	0.55	9	I
Elderberry.....	<i>Sambucus Cana- denis</i>	....	....	0.05	....	....	3.45	1	I
Huckleberry.....	<i>Gaylussacia resi- nosa</i>	0.00	0.02	0.00	0.51	0.84	0.70	8	I
Huckleberry.....	<i>Gaylussacia du- mosa</i>	0.02	0.04	0.03	0.37	0.65	0.49	3	I
Pigeonberry.....	<i>Phytolacca decan- dra</i>	....	....	0.02	....	....	5.00	1	I
Strawberry.....	<i>Fragaria Virgin- iana</i>	....	....	0.03	....	....	1.73	1	I
Teaberry.....	<i>Gaultheria procum- bens</i>	....	....	0.06	....	....	0.67	1	I
Miscellaneous plants—leaves only									
Azalea.....	<i>Azalea nudiflora</i>	....	....	0.08	....	....	0.78	1	I
Bay laurel.....	<i>Kalmia glauca</i>	....	....	0.19	....	....	0.45	1	IV
Bracken fern.....	<i>Pteris aquilina</i>	0.03	0.06	0.05	0.78	2.12	1.38	4	I
Brier.....	<i>Rosa canina</i>	....	....	0.08	....	....	1.07	1	I
Catbrier.....	<i>Smilax rotundi- folia</i>	....	....	0.02	....	....	1.28	1	I
Cattail.....	<i>Typha angusti- folia</i>	0.06	0.95	0.50	0.80	1.20	1.50	2	II or IV
Forsythia.....	<i>Forsythia suspensa</i>	....	....	0.06	....	....	1.98	1	I
Kudzu.....	<i>Pueraria Thun- bergiana</i>	....	....	0.09	....	....	2.25	1	I
Lilac.....	<i>Syringa vulgaris</i>	....	....	0.06	....	....	2.70	1	I
Marsh elder.....	<i>Iva frutescens</i>	1.50	2.04	1.77	1.17	1.22	1.19	2	IV
Moss.....	<i>Lycopodium</i> sp.	....	....	0.01	....	....	0.40	1	I
Peppermint.....	<i>Mentha piperita</i>	....	....	0.08	....	....	2.06	1	I
Pond lily, white....	<i>Castalia tuberosa</i>	....	....	0.36	....	....	0.92	1	IV
Pond lily, yellow....	<i>Nymphaea Kal- miana</i>	....	....	0.24	....	....	1.72	1	IV
Rose, wild.....	<i>Rosa humilis</i>	....	....	0.07	....	....	0.65	1	I
Salt wort.....	<i>Salsola Kali</i>	....	....	0.84	....	....	2.08	1	IV
Tamarix, leaves....	<i>Tamarix gallica</i>	....	....	1.05	....	....	1.40	1	IV
Tamarix, stem.....	<i>Tamarix gallica</i>	....	....	0.85	....	....	.41	1	IV

tago, Rumex, and Achillea had high contents of Na. Some species of these plants were found to accumulate Na only if it was present in relatively large

amounts in the nutrient substrate. Others were always high in Na, regardless of the growth medium. The first group included species of *Neslia*, *Plantago*, and *Achillia*, and the second group, species of *Rumex*. The range in Na values obtained was from 0.00 to 0.47 per cent. Weeds were found to be notably high in K, the values for this element ranging from less than 1 to a maximum of 5.75 per cent.

The leaves of eight berry plants were found to contain only very small amounts of Na. Those of the cranberry and the huckleberry were notably low in this element.

Of the miscellaneous plants, some contained only small amounts of Na, whereas others had accumulated large amounts. Examples of the first group included species of *Azalea*, *Pteris*, *Rosa*, and *Smilax*, and of the second group, species of *Kalmia*, *Typha*, *Iva*, *Castalia*, *Nymphaea*, *Salsola*, and *Tamarix*. *Castalia* and *Nymphaea*, which are water plants, contained fairly large amounts of Na. Only one plant of the miscellaneous group, the marsh elder, contained more Na than K. The average Na content of this plant was 1.77 per cent, whereas it contained only 1.19 per cent K.

Table 2 shows the Na and K contents of 21 common vegetables. Members of the *Chenopodiaceae*, *Cruciferae*, *Lilaceae*, and *Umbelliferae* were found to contain relatively large amounts of Na. All of the vegetables, with the exception of peas, lima beans, potatoes, and tomatoes, appeared to have considerable capacity to absorb Na if it was available to them. Of all the plants tested, table beets showed the greatest concentration of Na, the leaves containing up to 3.00 per cent of the element.

It was found possible to check the Na-accumulating ability of certain plants by comparing their composition when grown on normal soils with that of the same species from salt-marsh or dune areas. Table 3 gives comparative data of this type for 10 plants. Blackberry, bracken fern, wild carrot, cherry, silver maple, and pine had a low Na content, whatever the medium in which they grew. Cattail, plantain, red clover, and yarrow tended to accumulate Na when growing on salt-marsh or dune areas.

A further check on the Na-accumulating ability of specific plants was found possible by comparing the composition of those grown on Na-treated and untreated soil. The results of this study are summarized in table 4. The data indicate that table beets, cabbage, cucumbers, Ladino clover, parsnips, and radishes accumulate Na to varying degrees. The data obtained with Ranger alfalfa were inconclusive.

The Na and K contents of some common salt-marsh plants are listed in table 5. Despite the fact that the hydrosphere, as reported by Clark, contains 28 times as much Na as K, only three of these plants, marsh elder, cattail, and dune grass, contained more Na than K.

The following tentative grouping<sup>4</sup> was made of the plants so far analyzed:

Type I—Plants that do not accumulate Na, even if present in large amounts in the nutrient substrate.

<sup>4</sup> The inclusion of any plant, among those listed, under a given type is tentative only since the decision was based on too few samples to warrant definite conclusions.

TABLE 2  
Na and K contents of some vegetables  
Dry-weight basis

COMMON NAME	PART ANALYZED	VARIETIES	Na			K			SAM- PLES ANA- LYZED	TYPE
			Mini- mum	Maxi- mum	Aver- age	Mini- mum	Maxi- mum	Aver- age		
			%	%	%	%	%	%		
Asparagus	Spears	All varieties	0.01	0.07	0.04	0.92	2.55	1.82	4	II
Broccoli	Flower	Calabrese	....	....	0.05	....	....	2.45	1	II or III
	Leaf	Calabrese	....	....	0.14	....	....	1.26	1	
	Stem	Calabrese	....	....	0.07	....	....	2.64	1	
	Stem	Calabrese	....	....	0.07	....	....	2.64	1	
Cabbage	Tops	All varieties	0.03	0.30	0.16	1.67	3.85	2.63	17	II
Carrots	Leaf	Chantenay	0.20	0.45	0.33	1.59	4.40	3.00	2	III or II
	Root	Chantenay	....	....	0.36	....	....	4.30	1	
	Stem	Chantenay	....	....	0.14	....	....	5.50	1	
	Stem	Chantenay	....	....	0.14	....	....	5.50	1	
Corn	Leaf		....	....	0.03	....	....	1.54	1	I
Cucumber	Leaf	National	0.03	0.12	0.07	1.77	2.10	1.93	2	I or II
	Leaf	Pickle								
Kohlrabi	Root	Early Purple Vienna	....	....	0.06	....	....	1.72	1	II or III
	Stem	Early Purple Vienna	....	....	0.14	....	....	4.35	1	
	Top	Early Purple Vienna	....	....	0.13	....	....	1.60	1	
	Top	Early Purple Vienna	....	....	0.13	....	....	1.60	1	
Lima beans	Leaf	King of Garden	....	....	0.00	....	....	2.00	1	I
Lettuce	Tops	Big Boston	....	....	0.04	....	....	2.17	1	II
	Tops	Great Lakes	0.10	0.28	0.16	2.28	5.06	4.08	8	
Parsnip	Tops	Hollow Crown	0.03	0.06	0.05	3.35	3.80	3.57	2	II
	Roots	Hollow Crown	0.11	0.28	0.19	2.40	2.75	2.57	2	
	Roots	Hollow Crown	0.11	0.28	0.19	2.40	2.75	2.57	2	
Peas	Berries	Shasta	....	....	0.03	....	....	0.88	1	I
	Leaf	Thomas	0.00	0.05	0.02	0.72	1.43	1.05	8	
	Leaf	Laxton								
	Pod	Shasta	....	....	0.01	....	....	0.85	1	
Pepper	Stem	Shasta	....	....	0.04	....	....	1.83	1	
	Leaf	Italian Sweet	....	....	0.01	....	....	3.45	1	I
	Leaf	Jersey	....	....	0.08	....	....	4.35	1	I
	Leaf	Yellow	....	....	0.08	....	....	4.35	1	
Potatoes, sweet	Stem	Jersey	....	....	0.09	....	....	4.00	1	
	Stem	Yellow	....	....	0.09	....	....	4.00	1	
Potatoes, white	Leaf	Katahadin	....	....	0.01	....	....	4.09	1	I
Radish	Tops	Early Scarlet Globe	0.30	0.48	0.39	3.00	3.45	3.22	2	III
	Roots	Early Scarlet Globe	0.20	0.44	0.31	5.25	6.30	5.77	2	
Snapbeans	Pods	Bountiful	0.05	0.11	0.09	1.14	2.95	1.91	7	I
Spinach	Tops	Savoy	0.30	0.61	0.42	2.40	8.88	6.09	3	III
Squash	Leaf	Early	....	....	0.03	....	....	4.00	1	I
	Leaf	Prolific	....	....	0.03	....	....	4.00	1	
Table beets	Tops	All varieties	0.39	3.00	1.74	5.52	6.63	6.20	5	III
	Roots	All varieties	0.18	0.44	0.31	2.78	3.11	2.94	2	
Tomato	Leaf	Rutgers	0.03	0.07	0.04	1.79	3.03	2.29	5	I
	Fruit	Rutgers	0.04	0.06	0.05	3.61	3.98	3.80	5	
Turnip	Leaf	Amber Globe	....	....	0.03	....	....	3.06	1	I

TABLE 3

*Na and K contents of plants growing on soil and on salt marshes or dunes*

Dry weight basis

COMMON NAME	SCIENTIFIC NAME	SOIL			MARSH OR DUNE AREAS		
		Na	K	Samples analyzed	Na	K	Samples analyzed
		%	%		%	%	
Blackberry.....	<i>Rubus villosus</i>	0.03	1.73	1	0.07	0.27	1
Bracken fern.....	<i>Pteris aquilina</i>	0.05	1.38	4	0.05	1.27	2
Wild carrot.....	<i>Daucus Carota</i>	0.03	2.99	5	0.05	2.50	1
Cattail.....	<i>Typha angustifolia</i>	0.06	1.20	1	0.80	0.95	1
Cherry.....	<i>Prunus Virginiana</i>	0.04	1.03	2	0.06	0.75	1
Maple.....	<i>Acer saccharinum</i>	0.04	1.13	2	0.03	0.68	1
Plantain.....	<i>Plantago lanceolata</i>	0.14	1.53	5	0.40	1.10	2
Pine.....	<i>Pinus Virginiana</i>	0.05	0.36	1	0.03	0.55	2
Red clover.....	<i>Trifolium pratense</i>	0.07	1.64	9	0.24	0.85	1
Yarrow.....	<i>Achillea Millefolium</i>	0.10	2.15	5	0.22	0.95	1

TABLE 4

*Na and K contents of plants grown with and without added Na\**

Dry-weight basis

COMMON NAME	PLANT PART ANALYZED	VARIETIES	NO Na			WITH Na		
			Na	K	Samples analyzed	Na	K	Samples analyzed
			%	%		%	%	
Alfalfa	Tops	All	0.05	1.70	30	....	....	.
	Leaves	Ranger	....	....	..	0.06	1.34	2
	Stem	Ranger	....	....	..	0.08	1.17	2
Beets, table	Tops	All	1.61	3.97	3	....	....	.
	Roots	All	0.24	0.92	1	....	....	.
	Tops	Detroit Dark Reds	0.90	6.45	1	3.00	6.63	1
	Roots	Detroit Dark Reds	0.18	3.11	1	0.44	2.78	1
Cabbage	Heads	All	0.21	2.69	11	....	....	.
	Heads	Marion Market	0.03	2.33	3	0.19	2.71	3
Cucumber	Leaves	National Pickle	0.03	1.77	1	0.10	2.10	1
Ladino clover	Tops	.....	0.16	1.82	22	0.24	1.58	1
Parsnip	Tops	Hollow crown	0.06	3.35	1	0.03	3.80	1
	Roots	Hollow crown	0.11	2.40	1	0.28	2.75	1
Radish	Tops	Early Scarlet Globe	0.30	3.00	1	0.48	3.45	1
	Root	Early Scarlet Globe	0.20	5.25	1	0.44	6.30	1

\* As NaCl.

Type II—Plants that accumulate Na if a sufficient amount is present in the nutrient substrate.

Type III—Plants that accumulate Na, even if the nutrient substrate is almost free of Na.

Type IV—Plants native to salt-marsh or dune areas that normally contain large amounts of Na.

Gradations existed among the first three types, and no definite line of demarcation could be drawn between them. Varietal differences often made a given species fall into more than one type. An example of this was Marion Market cabbage, classified as a type-II plant, notwithstanding the fact that cabbages, as a group, seemed to fit best into type III.

TABLE 5  
Na and K contents of salt-marsh plants  
Dry-weight basis

COMMON NAME	SCIENTIFIC NAME	Na	K	SAMPLES ANALYZED
		%	%	
Bay laurel.....	<i>Kalmia glauca</i>	0.09	0.45	1
Cattail.....	<i>Typha angustifolia</i>	0.95	0.80	1
Dune grass.....	<i>Sieglingia purpurea</i>	0.92	0.37	1
Marsh elder.....	<i>Iva frutescens</i>	1.77	1.19	2
Salt meadow grass.....	<i>Spartina patens</i>	0.31	0.39	3
Salt wort.....	<i>Salsola Kali</i>	0.84	2.08	1
Sedge.....	<i>Carex</i> sp.	0.22	0.86	2

It is also possible that, by adjusting the cation ratios in the nutrient medium, many low-Na plants could be induced to adsorb considerable amounts of Na, and preliminary data so indicate.

#### SUMMARY

Over 300 samples of plants, representing 77 species that are native to New Jersey and 24 varieties of cultivated plants, have been analyzed for Na. Their content of K was also determined.

The Na content of the wild plants varied between 0.00 and 2.04 per cent of their dry weight.

The Na content of the cultivated plants varied between 0.00 and 3.00 per cent of their dry weight.

The plants examined were divided into 4 types:

Type I—Plants that did not accumulate Na.

Type II—Plants that accumulated Na if it was present in abundance.

Type III—Plants that accumulate Na whether it was abundant or not.

Type IV—Plants, native to salt-marsh areas, that were normally high in Na.

The Na content of most plants was much lower than their content of K.



The Na content of certain species of *Typha*, *Sieglingia*, and *Iva* was higher than the content of K.

Of 15 grasses analyzed, only 4 contained more than 0.10 per cent Na. Dune grass and salt-meadow grass averaged 0.37 and 0.39 per cent Na, respectively.

The legumes, especially Ladino and red clovers, tended to contain somewhat higher percentages of Na than ordinary grasses.

None of the 15 deciduous trees showed any indication of being Na accumulators.

Of the common weeds, certain species of burdock, mustard, plantain, and yarrow had the highest Na content. The Na content of *Plantago lanceolata* varied between 0.00 and 0.47 per cent.

Weeds were found to be notably high in K, the average for two samples of burdock being 4.97 per cent.

Cranberry and huckleberry plants were notably low in Na, their averages being 0.01 and 0.00 per cent, respectively.

Of 21 common vegetables, cabbage, carrots, radishes, spinach, and beets contained the highest percentages of Na. The Na content of beet leaves varied between 0.39 and 3.00 per cent, with an average of 1.74 per cent for 5 samples.

By comparing the Na content of 10 species of plants when grown on normal soils and on salt-marsh or dune areas, it was found that only 4, cattail, plantain, red clover, and yarrow, tended to accumulate Na when the opportunity was presented.

When grown on normal soils with and without applications of Na, beets, cabbage, cucumbers, Ladino clover, parsnips, and radishes accumulated Na, but alfalfa did not.

## YIELD AND COMPOSITION OF FORAGE GROWN ON ONE CONNECTICUT FARM IN 1946<sup>1</sup>

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*Eastern States Farmers' Exchange*

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A survey of the analyses of hay as fed on farms of more than 150 members in nine Northeastern States by the Eastern States Farmers' Exchange showed a very wide range in chemical constituents, a high percentage of low calcium and cobalt determinations, and evidence of a lack of balance between calcium and magnesium and potassium. The farmers' purchasing cooperative that conducted the survey owns and operates a farm and feed research laboratory at Ellington, Connecticut. The question was raised as to how the roughage produced there for feeding trials compared with that being grown and used by members. The dairy herd was fed with roughage produced under a system of intensive grassland farming, with native pasture and combinations of grass and legumes used for grass silage, hay, and pasture. All of the long feed for the herd of 100 animals, including 50 milking cows available for feeding trials, was grown on the farm, besides 30 acres of permanent pasture and 32 acres of mixed Ladino seedings primarily for grass silage and pasture. All but 5 of the 131 acres were fenced to permit rotational grazing. The forage production was considered no greater than that of many members under a similar system of grassland management. The health of the herd was very satisfactory and the herbage of a quality to ensure high feed consumption.

A record of the manure, lime, and fertilizer usage for 9 years since the farm was purchased was available. Information was desired on the nutrient removals of forage under such intensive production. A joint project, therefore, between the Fertilizer and Feed Service, was initiated for at least a 2-year study of the chemical composition of all of the several types of feed produced on this farm. Data for the 1946 growing season and information concerning the soils and fertilizer practices associated with this production are presented in this paper.

### SOILS

Sixty per cent of the acreage of this farm is upland soil of the AT and ET types, derived from unstratified glacial till, Cheshire loam and stony loam (9, pp. 44, 49). The other acreage is lowland soil, developed from recent alluvial material, with open ditches to provide adequate drainage.

<sup>1</sup> Contribution from the Eastern States Farmers' Exchange, Inc., West Springfield, Massachusetts.

<sup>2</sup> Associated with the Fertilizer, Feed, and Control Laboratory respectively. Acknowledgment is made of the assistance given by P. A. Campbell and D. Wallace in the management of the fields and herd, to R. A. Mullany in obtaining the samples, to W. Flach for assistance with the analytical work, and to J. A. Chucka for criticism of the manuscript.

In 1938, an intensive study<sup>3</sup> of the most productive field, No. 10, yielded the following data:

Nitrogen..... 0.238 per cent      Base-exchange capacity....11.30 m. e.  
Organic carbon... 2.484 per cent      Lime requirement—Jones... 7,540

	TOTAL LBS. PER ACRE	AVAILABLE LBS. PER ACRE
Nitrogen.....	4,760	.....
Phosphorus.....	1,820	165—Truog laboratory method
Potassium.....	29,800	117—Ammonium acetate replacement
Calcium.....	....	1,878—Ammonium acetate replacement
Magnesium.....	....	218—Ammonium acetate replacement

Use of the 1-2-2 ratio of fertilizer for vegetable crops was recommended for this and similar soils.

Rapid soil tests with the Connecticut Universal System were made on the farm in 1938 and again in 1946, as shown in table 1. Soil test determinations are given as relative ratings on a scale of 1 to 10 as shown in the footnote. Samples of topsoil and subsoil for the 1946 tests were taken under each cage or ring after each cutting. During the 9 years between tests, the pH of these soils changed very little, although the replaceable calcium and magnesium improved. Leaching losses should have been slight because the soils were in sod except when in corn, in which domestic ryegrass was seeded at the last cultivation.

The phosphorus status improved on all fields. Consideration should be given to reducing the applications on the fields (1-W, 10, and 1-C) on which tobacco was grown before 1938. Permanent pasture, field 4, which showed little average change in available phosphorus had the widest range in pH, the highest active aluminum and manganese, and the lowest replaceable calcium of the upland soils.

The soils on which hay and grass silage have been harvested as a general practice showed little or no improvement in the status of exchangeable potassium. On the other hand, pasture 7, used exclusively for grazing young and dry stock, and field 8, predominantly Ladino clover used chiefly for grazing by the milking herd, showed marked improvement.

#### MANURE, LIME, AND FERTILIZER USAGE

Since 1938, the average yearly application per acre on the 131 acres has been seven spreader loads of manure, 530 pounds of ground limestone, and the equivalent of 280 pounds of a 6-13-12 mixed fertilizer. When the fields are grouped into five classifications of roughage usage, the average annual applications are as shown in table 2.

If the nutrients in manure are computed as 10-5-10 pounds of N-P<sub>2</sub>O<sub>5</sub>-K<sub>2</sub>O per load (1 ton), the total nutrients applied yearly per acre for the 9 years have been approximately 90 pounds N, 70 pounds P<sub>2</sub>O<sub>5</sub>, and 110 pounds K<sub>2</sub>O.

The average annual treatment for the last 5 years, since the farm has grown

<sup>3</sup> Made by the late Dr. M. F. Morgan, Connecticut Agricultural Experiment Station.

TABLE 1  
Soil Tests\*—Connecticut Universal System—1938 and 1946  
Average of soils under each roughage sample

FIELD NO.	NUMBER OF SAMPLES	TOPSOIL		SUBSOIL	Al	Fe	Mn	Mg	Ca	NNO <sub>2</sub>	P	K
		pH	pH range, from/to	pH								
Upland soils—1946												
1-W	9	5.7	5.2/5.9	5.7	2.6	1.0	T	10.0	6.7	5.2	7.3†	1.3
8	15	5.9	5.4/6.3	5.6	4.4	1.1	T	9.9	7.7	5.7	4.3	2.7
2	6	6.6	6.1/6.9	6.6	1.8	1.0	..	10.0	8.0	2.8	3.8	2.3
1-E	6	5.6	5.2/5.8	5.8	4.5	1.0	0.6	9.7	8.0	4.3	5.3†	1.2
6	9	5.8	5.4/6.7	5.9	2.7	1.0	T	8.9	7.6	2.1	4.0	1.4
3	9	6.2	5.7/6.6	6.1	3.3	1.0	T	10.0	5.9	2.2	3.3	1.1
1-EE	6	5.4	5.1/5.6	5.5	4.8	1.0	T	9.3	6.3	4.7	4.3†	1.0
10	6	5.8	5.8/6.1	5.7	4.3	1.0	1.5	9.0	8.5	2.7	9.0†	8.3
1-C‡	9	5.5	5.3/5.8	5.4	2.7	1.0	2.3	10.0	7.6	6.6	4.4†	3.3
4	15	5.7	5.1/6.2	6.4	6.5	1.0	1.3	9.0	4.4	4.7	2.1	2.4
7	15	5.8	4.9/6.3	5.3	6.6	1.0	T	7.1	3.4	2.6	2.6	3.7
Average.....		5.8		5.8	4.0	1.0	-1.0	9.3	6.7	4.0	4.6	2.6
Lowland soils—1946												
15	6	5.5	5.3/5.9	5.2	5.2	2.8	..	9.7	3.3	2.0	4.0	1.3
12-B	6	5.9	5.7/6.1	5.4	3.7	1.8	..	9.3	7.7	1.7	4.8	1.3
12-A	6	6.0	5.3/6.4	5.5	3.5	1.3	..	10.0	8.5	1.8	3.2	1.0
15-A	2	5.8	5.5/6.1	5.6	5.5	2.0	..	10.0	2.5	1.5	2.0	2.5
14	2	5.5	5.4/5.6	5.9	3.5	2.0	..	10.0	2.0	1.5	2.5	1.0
Average.....		5.7		5.5	4.3	2.0	..	9.8	4.8	1.7	3.3	1.4
Upland soils—1938												
1-W	3	6.0		5.8	5.7	1.0	1.3	9.3	1.5		4.0†	1.2
8	3	5.7		5.3	8.4	1.1	1.7	9.0	1.6		2.3	1.5
2	3	6.6		5.6	3.0	1.0	0.0	9.4	1.8		2.5	2.0
1-E	3	5.8		5.7	6.8	1.0	1.2	9.0	2.7		4.3†	1.0
6	3	5.9		5.5	5.8	1.3	0.8	8.5	3.8		1.5	1.3
3	3	6.1		6.1	5.3	1.0	0.5	9.3	1.6		2.6	2.0
10	3	5.7		5.8	6.8	1.0	2.8	9.2	2.0		6.0†	3.6
1-C	3	5.7			2.0	1.0	1.0	10.0	10.0		5.0†	4.0
4	3	6.4			5.3	1.0	0.0	8.7	6.0		2.3	1.3
7	3	5.1			9.5	1.0	1.5	6.0	1.5		1.0	2.3
Average.....		5.9			5.9	1.0	1.1	8.0	3.3		3.2	2.0
Lowland soils—1938												
12-B	3	5.4			4.0	3.0	2.0	6.0	4.0		4.0	3.0
12-A	3	5.4			2.0	2.0	..	8.0	8.0		1.0	2.0

\* Relative ratings of soil test determinations: 10 = very high; 8 = high; 6 = medium high; 4 = medium; 2 = low; 1 = very low; T = trace; 0 = --.

† Tobacco grown on land before 1938.

‡ Taken October, Ryegrass.

all the roughage used, has been 70 pounds of superphosphate and 400 pounds of mixed fertilizer, equivalent to an 8-12-13 mixture. For each of the 100 animals in the herd, this represents the use of about 100 pounds of superphosphate and 500 pounds of an 8-12-13 mixture at a cost of \$7.43 per animal. The annual application of 550 pounds of limestone per year cost \$1.80, or a total outlay of \$9.23 per animal for lime and fertilizer, not including the fertility brought on the farm in the feed bags.

For the 1946 crops, all of the fertilizer was applied to hay and pasture sods during October and November, 1945. Corn and new seedings were manured and a starter fertilizer was applied with the planter and drill in 1946. The applications of manure, limestone, and fertilizer used for the 1946 crops are shown in table 3. With restrictions in supply, the grades used in several instances were not those recommended for the conditions.

TABLE 2

*Average annual applications of manure, limestone, and fertilizer per acre, 1938-1947*

	ALFALFA	MIXTURES WITH ALFALFA	MIXTURES WITH LADINO (UPLAND)	MEADOWS AND MIXTURES WITH LADINO	PERMANENT PASTURE	AVERAGE ALL FIELDS
Ground limestone. .... lbs.	480	450	310	250	630	530
Manure..... loads	8	9	10	14	2	7
Fertilizer..... lbs.	250	280	280	170	310	280
Average Fertilizer Analysis...	3-12-20	4-13-17	6-14-13	4-15-9	9-12-11	6-13-12
Approximate Fertilizer Ratio..	1-4-7	1-3-4	1-2-2	1-4-2	1-1-1	1-2-2

## WEATHER DATA

The mean monthly precipitation and temperature and total hours of sunshine at the nearest U. S. Department of Commerce Weather Bureau Station, Hartford, Connecticut, from October, 1945 to September, 1946 were as follows:

MONTH	PRECIPITATION	TEMPERATURE	TOTAL SUN- SHINE	SNOWFALL (UNMELTED)
1945	inches	°F.	hours	inches
October.....	2.09	51.0	179	
November.....	5.81	42.4	101	9.9
December.....	6.85	24.0	135	18.2
1946				
January.....	2.72	26.4	150	10.2
February.....	2.81	25.6	172	13.5
March.....	1.84	45.7	289	0.0
April.....	2.58	46.6	242	0.9
May.....	5.87	57.1	246	
June.....	2.99	66.8	325	
July.....	4.84	71.6	303	
August.....	6.76	67.5	237	
September.....	2.36	65.7	234	



## METHODS OF SAMPLING AND ANALYSIS

To obtain yield data on the dry matter produced on the permanent pastures, clippings were made at 2-inch height under three 3-foot by 4-foot cages set up on each field. Three ring samples of 3/10,000-acre areas were cut before each harvest or grazing on the other fields. Sixteen fields were sampled. Samples of corn silage in triplicate were taken from the center row of five 30-foot rows and separated into stalks and ears. Quarter-inch slices from 1-foot intervals of the stalks and from the middle of each ear were made with a guillotine feed cutter and the composite samples frozen with dry ice for transportation to the labora-

TABLE 3  
*Manure, limestone, and fertilizer applied for 1946 crops*

FIELD NO.	TYPE OF MIXTURE	STABLE MANURE SPREADER LOADS	GROUND LIME- STONE	FERTILIZER ANALYSIS	ACRE RATE	DATE APPLIED, FALL 1945, SPRING 1946
			<i>cwt.</i>		<i>lbs.</i>	
1-W	Alfalfa, some Kentucky blue grass			5-15-20	260	10/15
8	Ladino-brome-timothy			10-10-10	390	11/1
2	Ladino-alfalfa-timothy			5-15-20	260	11/1
1-E	Ladino-timothy		25	5-15-20	260	10/14
6	Brome-Ladino-alfalfa			10-10-10	335	10/15
3	Brome-Ladino-alfalfa			10-10-10	285	11/16
1-EE	Timothy-alfalfa-Ladino		41	5-15-20	260	10/14
10	Oat silage	25	35	5-15-20	200	4/1
				Borax	20	
1-C	Corn	25		8-24-8	170	5/23
4	Permanent pasture			10-10-10	770	11/16
7	Permanent pasture		21	10-10-10	580	10/21
15	Ladino-timothy-red clover	10	17	None		10/15
12-B	Timothy-Ladino-red clover			10-10-10	310	10/18
12-A	Timothy-brome-Ladino			10-10-10	255	10/16
15-A	Reed canary grass	10	17	None		
14	Permanent pasture		35	10-10-10	300	10/7

tory. Three ring samples of domestic ryegrass were taken from each center corn row on October 28. All but the corn silage samples were dried promptly with heated air on trays of an egg incubator. After drying, all samples were stored at room temperature, no effort being made to preserve the carotene content by refrigeration.

The triplicate samples of each cutting were composited and analyses of the several cuttings made. The data presented are the weighted average analysis of all cuttings from each field.

Feed and fertilizer constituents were analyzed at the control laboratory of the Eastern States Farmers' Exchange at Buffalo, New York. The A.O.A.C. methods of 1945 were used for all but cobalt and copper determinations, which were made by a modified Marston and Dewey method (10).

Sodium determinations by flame photometer were made of weighted composite samples of hay and pasture by the New Jersey Agricultural Experiment Station.

TABLE 4  
*Field record—Westbrook Farm—1946*

FIELD NO.	ACRES	NUMBER OF CUTTINGS			TYPE OF ROUGHAGE	
		Pas- ture	Hay or silage	Total	Predominate	Others in order of stand
Upland soils						
1-W	4.5	0	3	3	Alfalfa	Some Kentucky bluegrass
8	2.3	5	0	5	Ladino	Smooth brome, timothy
2	10.0	1	1	2	Ladino	Alfalfa, timothy
1-E	5.0	0	2	2	Ladino	Timothy, witch grass, (Agropyron repens), Kentucky bluegrass, alfalfa
6	4.8	2	1	3	Smooth brome	Ladino, alfalfa
3	3.5	2	1	3	Smooth brome	Ladino, alfalfa, timothy
1-EE	2.6	0	2	2	Timothy	Alfalfa, Ladino, witch grass
10	9	0	1	1	Oat silage	Alfalfa seeded with oats
1-C	3.4	0	1	1	Silage corn	Ill. 448 @16,230 plants per acre 27.94 tons green weight
1-C		0	1	1	Domestic ryegrass	40 lbs. seeded last cultivation of corn
4	13.5	4	0	4	Kentucky bluegrass	White clover, bent
7	15.0	5	0	5	Kentucky bluegrass	White clover, bent, timothy
Lowland soils						
15	23.5	3	0	3	Ladino	Timothy, red clover
12-B	5.5	1	1	2	Timothy	Ladino, red clover
12-A	5.5	1	1	2	Timothy	Smooth brome, Ladino, Kentucky bluegrass
15-A	1	2	0	2	Reed canary grass	
14	1.6	2	0	2	Kentucky bluegrass	White clover, bent

The field designation, acreage, number of cuttings, and classification of herbage in order of visual predominance of legumes and grasses in the stand on the tillable fields are given in table 4.

## CHEMICAL COMPOSITION OF ROUGHAGE

The routine feed and fertilizer constituents of the crops grown on each field are included in table 5. The high acre yield of dry matter and protein ( $N \times 6.25$ )

TABLE 5  
*Feed and fertilizer constituents of roughage 1946*  
Weighted averages all cuttings

FIELD NO.	PER CENT OF DRY MATTER						CAROTENE M UNITS PER LB.	POUNDS PER ACRE						
	H <sub>2</sub> O	Ash	Protein	Fat	Fiber	Carbohydrate		Dry matter	Protein	N	P <sub>2</sub> O <sub>5</sub>	K <sub>2</sub> O	CaO	MgO
Upland soils														
1-W	8.52	6.46	16.64	1.66	14.86	66.45	63	10,248	1705	273	82	292	118	49
8	8.07	7.28	22.58	2.85	20.50	57.87	113	7,344	1658	265	69	303	74	39
2	8.45	7.95	15.23	2.20	27.84	66.17	96	6,585	1003	160	45	205	87	33
1-E	8.50	5.95	13.22	1.86	28.84	70.46	80	9,602	1270	203	56	201	88	44
6	8.08	6.60	13.12	2.35	30.58	69.85	117	8,563	1124	180	65	244	71	24
3	8.76	5.63	11.38	2.02	31.09	72.22	96	9,521	1083	174	60	214	69	33
1-EE	8.52	5.24	13.85	2.05	31.51	74.00	77	10,865	1107	177	59	226	80	35
10	8.47	7.67	11.70	2.25	31.25	69.91	192	6,300	737	118	41	236	25	29
1-C*	79.00	0.93	1.74	0.46	4.88	18.05	...	...	973	151	..	...	..	..
1-C	6.45	13.28	16.93	3.45	16.13	59.70	123	2,481	420	67	23	118	15	10
4	8.08	8.80	22.65	3.04	20.10	57.42	129	5,583	1264	202	51	146	61	26
7	8.32	6.93	18.30	3.14	22.61	63.31	107	6,442	1179	189	51	208	39	26
Lowland soils														
15	7.73	8.72	19.89	2.75	20.14	60.91	99	4,065	808	129	28	117	46	19
12-B	7.91	6.02	8.76	1.96	32.96	75.36	69	9,980	874	140	56	238	58	24
12-A	8.24	5.55	8.66	1.96	32.64	75.58	100	8,708	754	121	42	176	47	19
15-A	7.47	10.20	13.25	2.70	26.30	66.40	48	2,656	352	56	26	77	11	11
14	7.05	12.10	16.25	3.30	18.90	61.30	100	1,794	291	47	17	54	22	12
Range in analyses among individual cuttings														
Low.....	4.25	5.80	1.60	17.60	50.40	25	813	162	26	8	20	5	3	
High.....	13.28	30.00	4.30	35.90	79.90	218	9,531	863	138	49	195	67	30	

\* Corn.

and the corresponding acre removals of fertilizer constituents emphasize the high production under this intensive system of management.

TABLE 6  
Average content of chemical elements in dry matter of roughage  
Weighted averages all cuttings

FIELD NO.	TYPE OF MIXTURE	K	Na	Ca	Mg	Mn	Fe	Co	Cu	B	P	N	ASH	H <sub>2</sub> O
		%	%	%	%	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	%	%	%	%
Upland soils														
1-W	Alfalfa, some Kentucky bluegrass	1.87	.09	0.82	.29	35	197	.05	6	30	.35	2.66	6.46	8.52
8	Ladino-brome-timothy	2.86	.10	0.72	.32	51	193	.06	8	25	.41	3.61	7.28	8.45
2	Ladino-alfalfa-timothy	2.58	.06	0.94	.30	32	155	.07	7	29	.30	2.44	7.95	8.07
1-E	Ladino-timothy	1.73	.08	0.66	.28	60	296	.07	9	22	.26	2.11	5.95	8.50
6	Brome-Ladino-alfalfa	2.03	.15	0.59	.17	70	171	.05	9	20	.33	2.10	6.60	8.08
3	Brome-Ladino-alfalfa	1.87	.08	0.51	.21	41	473	.05	8	24	.27	1.82	5.63	8.76
1-EE	Timothy-alfalfa-Ladino	1.73	.18	0.53	.19	70	139	.06	7	21	.24	1.63	5.24	8.52
10	Oat silage	3.12	.09	0.28	.28	37	99	.04	5	21	.29	1.87	7.67	8.47
1-C	Corn*	1.73	...	0.26	.22	26	110	.07	7	8	.19	1.41	5.15	7.45
1-C	Domestic rye-grass	3.94	...	0.44	.24	74	891	.13	5	10	.41	2.71	13.28	6.65
4	Permanent pasture	2.17	.17	0.78	.28	109	432	.07	9	17	.40	3.63	8.80	8.08
7	Permanent pasture	2.32	.02	0.43	.24	79	198	.05	8	13	.34	2.93	6.93	8.32
Lowland soils														
15	Ladino-timothy-red clover	2.38	.07	0.81	.28	119	523	.05	9	24	.31	3.18	8.72	7.73
12-B	Timothy-Ladino-red clover	1.98	.01	0.41	.14	30	73	.05	6	13	.24	1.40	6.02	7.91
12-A	Timothy-brome-Ladino	1.68	.11	0.39	.13	42	884	.06	8	15	.21	1.39	5.55	8.24
15-A	Reed canary grass	2.40	.36	0.31	.24	132	133	.02	11	8	.43	2.12	10.20	7.45
14	Permanent pasture	2.50	...	0.86	.42	140	750	.13	10	19	.41	2.60	12.10	7.05

\* 1946 analyses not completed. Data given for mineral analysis 1945 crop—same variety, same treatment on adjacent field 10.

TABLE 6—Continued

FIELD NO.	TYPE OF MIXTURE	K	Na	Ca	Mg	Mn	Fe	Co	Cu	B	P	N	ASH	H <sub>2</sub> O
		%	%	%	%	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	%	%	%	%
Lowland soils—Continued														
Range all cuttings— low.....	1.43	.01	0.26	.10	21	38	.02	4	7	.18	0.93	4.25		
Range all cuttings— high.....	3.99	.36	1.13	.47	140	1688	.14	12	38	.52	4.80	13.28		
Mean all fields.....	2.28	.11	0.57	.25	67	336	.06	8	19	.32	2.33	7.61		
Average many feed crops.....	2.14	.70	0.88	.31	101	251	...	11	39	.34	2.63			
Average grass hays.....	2.09	...	0.57	.24	...	...	...	..	..	.26	1.36			
Average legume hays....	2.05	...	1.30	.32	...	...	...	..	..	.26	2.57			

The hay fields seeded with alfalfa, alone or in mixtures, produced the most dry matter, though the upland fields that were pastured exclusively—fields 8, 4, and 7—produced almost as much protein per acre. Moreover, these upland pastures produced more protein per acre than the 28 tons of corn silage grown on field 1-C.

Attention is directed to the high acre removals of potassium ( $K_2O$ ) from fields 6, 3, 1-EE, 12-B and 12-A, in a well-balanced combination of smooth brome or timothy with Ladino clover; that is, the first cutting taken for hay and thereafter grazed. The high potash removals point to the quantities of the nutrient in transit from and to the fields through the barn and the greater chances of losses in handling the manure.

#### *Chemical elements in dry matter*

The average contents of eleven chemical elements in the dry matter grown on these fields during 1946 are shown in table 6. The metallic constituents are arranged in order of the relative strength of ions as suggested by Cooper (5). For comparative purposes the average composition of many feed crops (4) and of grass and legume hays (5, p. 33) as given by Cooper is also presented.

The same analyses calculated as milliequivalents per 100 gm. of dry matter, arranged in order of the calcium content, are given in table 7.

#### *Evaluation of roughage for cattle*

One purpose of this study was to find out whether the roughage grown on this feed research farm was representative, in chemical constituents, of that grown on members' farms. Comparison of the average analyses and range between roughage taken from the field and from the manger on Westbrook Farm and that taken from members' farms as fed is shown in table 8. The approximate requirement of dairy cattle per pound of total feed intake, which the Eastern States



Feed Research Department uses as a general guide in the evaluation of roughage for dairy cattle is likewise given for comparison.

The averages for the roughage as fed on the research farm are higher in nitrogen, calcium, and potassium and lower in cobalt than the usual values for rough-

TABLE 7

*Chemical elements in dry matter of roughage*

Calculated as milliequivalents per 100 gm.—weighted average all cuttings arranged in order of calcium content

FIELD NO.	TYPE OF ROUGHAGE	K	Na	Ca	Mg	Mn	Fe	Co	Cu	B	P	N*	SUM OF K, Na, Ca, Mg
<i>Seeded fields</i>													
2	Ladino-alfalfa-timothy	66	3	47	25	0.12	0.55	.0002	.022	0.80	29	523	140
1-W	Alfalfa-some Kentucky bluegrass	48	4	41	24	0.13	0.71	.0002	.018	0.83	34	570	117
15	Ladino-timothy-red clover	61	3	40	23	0.43	1.87	.0002	.028	0.66	30	681	127
8	Ladino-brome-timothy	73	4	36	26	0.19	0.69	.0002	.025	0.69	40	773	140
1-E	Ladino-timothy-alfalfa	44	3	33	23	0.22	1.06	.0002	.028	0.61	25	452	104
6	Brome-Ladino-alfalfa	52	7	29	14	0.25	0.61	.0002	.028	0.55	32	450	102
1-EE	Timothy-alfalfa-Ladino	44	8	26	16	0.25	0.50	.0002	.022	0.58	23	349	94
3	Brome-Ladino-alfalfa	48	3	25	17	0.15	1.69	.0002	.025	0.66	26	390	94
12-B	Timothy-Ladino-red clover	51	0	20	12	0.15	0.26	.0002	.019	0.36	23	300	83
12-A	Timothy-brome-Ladino	43	5	19	11	0.15	3.16	.0002	.025	0.42	20	298	78
15-A	Reed canary	61	16	15	19	0.48	0.47	.0001	.033	0.22	42	557	112
10	Oat silage	80	4	14	23	0.13	0.35	.0001	.015	0.58	28	400	121
1-C	Domestic rye grass	78	..	22	20	0.27	3.19	.0004	.016	0.28	40	580	...
1-C	Ensilage corn (1945) crop	44	..	13	18	0.10	0.39	.0002	.020	0.22	18	302	...
<i>Permanent pastures</i>													
14	Bluegrass	64	..	42	35	0.51	2.69	.0004	.030	0.53	40	660	141
4	Bluegrass	56	7	39	23	0.40	1.55	.0002	.028	0.47	39	777	125
7	Bluegrass	59	1	21	20	0.29	0.71	.0002	.025	0.36	33	627	101
<i>Range in Average analyses</i>													
Low.....		37	0	13	8	0.08	0.14	.00007	.013	0.19	17	200	...
High.....		102	16	56	39	0.51	6.05	.00050	.038	1.05	50	1030	...

\* Valence of 3.

age from members' farms. With the possible exception of cobalt on the research farm, the roughages from both sources adequately meet the standard requirements per pound of total feed intake.

During the fall and winter, 12 samples of silage and hay as fed on the research farm were taken and analyzed. The results are given in table 9, with the average

TABLE 8

Range in analysis of roughage from field and as fed compared with hay as fed from members' farms, and approximate requirements of dairy cattle based on total feed intake

	WESTBROOK LABORATORY FARM						FROM MEMBERS' FARMS			APPROXIMATE REQUIREMENT BASED ON TOTAL FEED INTAKE
	From Field			As Fed			As Fed			
	Low	Avg.	High	Low	Avg.	High	Low	Usual	High	
Protein										
<i>per cent</i>	6.00	14.00	30.00	6.85	10.69	14.75	6.00	8.0-10.0	23.00	10.00
Ca..... <i>per cent</i>	0.26	0.57	1.13	0.29	0.41	0.86	0.20	0.3- 0.4	2.10	0.3-0.35
P..... <i>per cent</i>	0.18	0.32	0.52	0.23	0.25	0.31	0.13	0.3	0.51	0.2-0.25
Mg..... <i>per cent</i>	0.10	0.25	0.47	0.11	0.17	0.29	0.12	0.25-0.5	0.63	0.05 or less
K..... <i>per cent</i>	1.43	2.28	4.00	1.44	2.01	2.29	0.90	1.0- 2.0	6.00	0.1*
Mn..... <i>p.p.m.</i>	21.00	67.00	140.00	20.00	47.00	72.00	11.00	50-100.0	400.00	30-50*
Co..... <i>p.p.m.</i>	0.02	0.06	0.14	0.02	0.04	0.08	0.01	0.1	0.19	0.06
Cu..... <i>p.p.m.</i>	4.00	8.00	12.00	4.00	6.00	9.00	4.00	10.0	14.00	5.00
Fe..... <i>p.p.m.</i>	38.00	336.00	1688.00	50.00	69.00	95.00	50.00	100.0	331.00	30-50*
Carotene										
<i>M units/lb.</i>	2.50	106.00	218.00	1.60	7.00	25.00	0	3-8	82.00	5.00

\* Dairy cattle requirements not established—calculated from other animals.

TABLE 9

Average chemical composition of dry matter of silage and hay as fed, fall, 1946-winter, 1947

	AVERAGE ANALYSIS		SILAGE			HAY									
	From field*	Hay as fed	Grass	Corn	Corn	Al- falfa for cal- ves	Brome 2nd cutting	Tim- othy mix- ture	Brome mix- ture	Tim- othy mix- ture	Brome mix- ture, mow 1	Clo- ver mix- ture, mow 2	Tim- othy mix- ture, mow 3	Tim- othy mix- ture, mow 4	
Month and year.....			3-47	3-47	11-46	10-46	10-46	10-46	2-47	2-47	3-47	3-47	3-47	3-47	
Moisture..... <i>per cent</i>			71.60	70.00	6.25†	10.25	9.40	9.50	7.70	7.60	5.65	5.75	6.05	5.95	
Ash..... <i>per cent</i>			2.80	1.50	4.75	5.10	5.50	5.20	5.40	6.40	5.30	5.90	5.80	6.00	
Protein..... <i>per cent</i>			4.70	2.70	6.80	14.75	9.20	6.85	9.60	8.60	13.75	13.55	10.20	10.10	
Fat..... <i>per cent</i>			1.10	0.60	2.20	1.60	1.80	1.80	2.20	2.40	1.40	1.30	1.90	1.50	
Fiber..... <i>per cent</i>			10.45	9.85	23.00	29.50	35.10	36.20	34.30	34.70	36.90	36.30	33.30	34.50	
Carbohydrates..... <i>per cent</i>			19.80	25.20	80.00	68.30	74.10	76.65	75.10	75.00	73.90	73.50	76.05	76.45	
Carotene..... <i>M units/lb.</i>			25.00	15.00	3.70	10.50	3.50	6.00	7.00	1.60	1.67	2.33	4.00	5.00	
N..... <i>per cent</i>	2.33	1.71	0.75	0.43	1.09	2.36	1.47	1.09	1.54	1.38	2.20	2.17	1.63	1.62	
P..... <i>per cent</i>	0.32	0.25	0.09	0.04	0.24	0.31	0.28	0.23	0.27	0.23	0.24	0.26	0.24	0.25	
K..... <i>per cent</i>	2.28	2.01	0.69	0.39	1.33	1.44	2.22	1.63	2.22	2.17	2.29	2.23	1.95	1.98	
Ca..... <i>per cent</i>	0.57	0.41	0.30	0.20	0.21	0.86	0.29	0.30	0.29	0.39	0.30	0.29	0.47	0.49	
Mg..... <i>per cent</i>	0.25	0.17	0.08	0.07	0.20	0.29	0.11	0.17	0.11	0.16	0.12	0.14	0.18	0.21	
Cl..... <i>per cent</i>	....	0.43	0.09	0.06	0.15	0.15	0.24	0.72	0.24	1.12	0.21	0.49	0.36	0.36	
B..... <i>p.p.m.</i>	19	12	12	6	7	29	6	5	6	8	15	13	19	11	
Mn..... <i>p.p.m.</i>	67	47	14	7	16	24	66	20	72	34	59	70	26	52	
Co..... <i>p.p.m.</i>	0.06	0.04	0.02	0.06	0.03	0.02	0.05	0.03	0.06	0.08	0.05	0.05	0.05	0.02	
Cu..... <i>p.p.m.</i>	8	6	2	2	6	4	6	8	6	6	5	5	6	9	
Fe..... <i>p.p.m.</i>	336	69	204	160	170	95	63	50	58	73	60	75	65	83	

\* From table 6.

† Moisture in green silage 71.6 per cent.

analysis of the field samples from table 6 for comparison. The high proportionate loss of calcium and magnesium and the low loss of potassium point to a high loss of leaves in the harvesting operations with side delivery rake, loader, and forks.

TABLE 10

*Ratios of chemical elements in roughage*

Percentage of dry matter, weighted averages of all cuttings arranged in order of calcium content

FIELD NO.	N/P	N/Ca	N/Mg	P/Mg	K/N	K/P	K/Mn	Mg/K	Ca/K	Ca/P	Ca/Mg	Ca/B	Ca/Mn	Fe/Mn	K+Na Ca+Mg
<i>Upland soils</i>															
1-W	7.60	3.24	9.17	1.20	0.70	5.34	534	.16	.43	2.34	2.83	273	234	5.63	1.77
8	8.80	5.01	11.28	1.28	0.79	6.98	561	.11	.25	1.75	2.25	288	141	3.78	2.85
2	8.13	2.60	8.13	1.00	1.06	8.60	806	.12	.36	3.13	3.13	324	294	4.84	2.13
1-E	8.12	3.20	7.54	0.93	0.82	6.65	288	.16	.38	2.54	2.36	300	110	4.93	1.93
6	6.36	3.56	12.35	1.94	0.97	6.15	290	.08	.29	1.79	3.47	295	84	2.44	2.87
3	6.74	3.57	8.67	1.28	1.03	6.93	456	.11	.27	1.89	2.43	213	124	11.54	2.71
1-EE	6.79	3.08	8.58	1.26	1.06	7.21	247	.11	.31	2.21	2.79	252	76	1.99	2.65
10	6.45	6.68	6.67	1.03	1.67	10.76	843	.09	.09	0.97	1.00	133	76	2.68	....
1-C*	7.42	5.42	6.41	.86	1.23	9.11	665	.13	.15	1.37	1.18	325	100	4.23	....
1-C	6.61	6.16	11.29	1.71	1.45	9.61	532	.06	.11	1.07	1.83	440	59	12.04	....
4	9.08	4.65	12.96	1.43	0.60	5.43	199	.13	.36	1.95	2.79	458	72	3.96	2.21
7	8.62	6.81	12.21	1.41	0.79	6.82	294	.10	.19	1.26	1.79	330	54	2.51	3.49
<i>Lowland soils</i>															
15	10.26	3.93	11.36	1.11	0.75	7.68	200	.12	.34	2.61	2.89	338	68	4.39	2.25
12-B	5.83	3.41	10.00	1.71	1.41	8.25	660	.07	.21	1.71	2.93	315	137	2.43	3.67
12-A	6.62	3.56	10.69	1.61	1.21	8.00	400	.08	.23	1.86	3.00	260	93	21.05	3.44
15-A	4.93	6.84	8.83	1.79	1.13	5.58	182	.10	.13	0.72	1.29	388	23	1.00	5.02
14	6.34	3.02	6.19	0.98	0.96	6.10	179	.17	.34	2.10	2.05	453	61	5.36	....
<i>Range in ratios</i>															
High.....	10.26	6.84	12.96	1.94	1.67	10.76	843	.17	.43	3.13	3.47	458	294	21.00	5.02
Low.....	4.93	2.60	6.19	0.86	0.60	5.43	179	.06	.11	0.72	1.00	133	23	1.00	1.77

\* Ensilage corn.

*Ratios of chemical elements in roughage*

Several ratios of chemical elements from table 6 are shown in table 10. The ratios of the sum of the monovalent potassium and sodium to the sum of the

divalent calcium and magnesium are given because of the possible relationships to milk fever and grass tetany, as suggested by Caldwell and Hughes (3). All ratios are calculated from average analyses of several cuttings.

The wide variations in proportions of elements found in forage from these fields suggest that the combined use of hay, silage, and pasture that vary so between species and composition may be very desirable to ensure that the dairy animals receive an adequate and uniform quantity and proportion of minerals. Alfalfa and Ladino mixtures that have 200 times as much calcium as manganese may present quite a different problem in manganese nutrition from that of reed canary grass with only 23 times as much calcium as manganese. The data show that the ratios of Ca/P vary fourfold and the ratios of Ca/Mn more than twelvefold, whereas the N/P, N/Mg, P/Mg, and K/P differentials are much narrower.

#### DISCUSSION

Liming practices on this farm have been directed toward maintaining a pH of approximately 6 for the efficient use of applied nutrients. Although the replaceable calcium has increased with the constant ground cover, the calcium in the forage with a high proportion of alfalfa or Ladino clover is considered low both in the field and as fed (6).<sup>4</sup> The calcium-potash ratio in alfalfa from field 1-W was 0.43, the highest found in any of the fields. This was lower than the 0.96 ratio Hunter, Toth, and Bear (7) found in alfalfa grown on soil with a calcium-potash ratio of 4 to 1, which was considered optimum for that experiment. Ten of the fields had more potash in relation to calcium than the 0.24 calcium-potash ratio shown by Albrecht (1, p. 16) for plants growing on highly developed soils. More calcium in relation to potash in the plants is indicated for more economical production. The correction for this condition is considered to be a moderate reduction in the amount of potash used, application of potash after the first cutting of mixtures that are largely alfalfa, and band application of part of the limestone used at seeding. In all of the fields the percentage of calcium in the second cutting was greater than that in the first, and there was a definite trend for calcium to increase throughout the season, as shown by Archibald (2), with plots fertilized and grazed intensively.

The data indicate that, with the annual use of 100 pounds of superphosphate in the stable for each animal in the herd, the amount of phosphorus used on the permanent pastures and fields previously in tobacco may well be decreased.

The use of 25 pounds of borax at seeding seemed adequate, because symptoms of boron deficiency have not been seen since borax was used.

The low magnesium found in brome and timothy mixtures on fields 6, 1-E, 12-A, and 12-B is associated with high magnesium in the soil tests. This suggests a scrutiny of the short-test method used for this element.

Of the sixteen fields sampled, 74 per cent of the cuttings had 0.06 p.p.m. or less of cobalt. This is considered the tentative threshold value in roughage for dairy cattle. Domestic ryegrass on the upland soil and permanent pasture on

<sup>4</sup> Unpublished data by W. G. Colby, Massachusetts Agricultural Experiment Station, on roughage analyses of plots 23 and 29, 1942.

the lowland soil had the highest content of cobalt. These were the only fields with cobalt content higher than the 0.08 p.p.m. reported by Mitchell (8) to be necessary to ensure complete animal health. Forty per cent of the samples had less cobalt in the first cutting. Symptoms of cobalt deficiency were not shown by the animals, but the grain ration was supplemented with cobalt.

#### SUMMARY

Analysis of samples of hay as fed on 150 farms in nine Northeastern States showed a very wide variation in chemical composition; a high proportion of the samples were low in calcium and cobalt, and there was a wide range in ratio of calcium to phosphorus and potassium.

Two questions were raised by this survey: (a) Was the roughage used for dairy cattle feeding experiments on one farm conducting feed research representative of that fed on farms such as were included in the survey? (b) What quantity of fertilizer nutrients was removed from the soil under very intensive grassland farming, with the land used for triple-purpose production of silage, hay, and pasture?

Samples of roughage used for silage, hay, and pasture from sixteen fields on this feed research farm in Connecticut taken during the 1946 season were analyzed for feed and fertilizer constituents, including sodium, cobalt, manganese, copper, and iron.

A record of the usage of manure, lime, and fertilizer had been kept. The average yearly application per acre for 9 years preceding the sampling was seven loads of manure, 530 pounds of limestone, and the equivalent of 280 pounds of 6-13-12 fertilizer.

A comparison of soil tests made at the beginning and at the end of this period showed little change in pH or potassium but considerable improvement in the status of calcium, phosphorus, and active aluminum.

Analyses of feed and fertilizer constituents were made of each harvest or grazing from sixteen fields, and the weighted average analysis of all samplings for each field was computed. The average chemical composition of eleven elements, arranged according to the relative strength of ions, was calculated as percentage composition and as milliequivalents in the dry matter.

Alfalfa mixtures produced the most dry matter in more than 5 tons of hay. Ladino clover-grass pasture that yielded  $3\frac{1}{2}$  tons of dry matter produced nearly as much total protein; that is, 1600 pounds per acre. Native pasture on upland soil yielded 3 tons of dry matter and nearly 1,200 pounds of protein.

More than 200 pounds of potassium ( $K_2O$ ) per acre was removed annually from twelve of the thirteen fields that had been under intensive grassland management for over 5 years. This emphasizes that the gains in production from such intensive fertilization and management may be associated with greater chances of losses of nutrients in the handling of both the forage and the manure.

Data on the composition of these roughages indicate in general that (a) the calcium content of legume mixtures is low in relation to potassium and phosphorus, (b) the magnesium content of hays in which grass predominated is lower



than that of mixtures in which Ladino was more evident, (c) native permanent, reed canary grass pasture and domestic ryegrass used as a cover crop after corn had the highest content of manganese, and mixtures high in alfalfa the lowest manganese, (d) cobalt is lower than is considered necessary for satisfactory animal health. The advisability of supplementing the grain ration with cobalt is indicated.

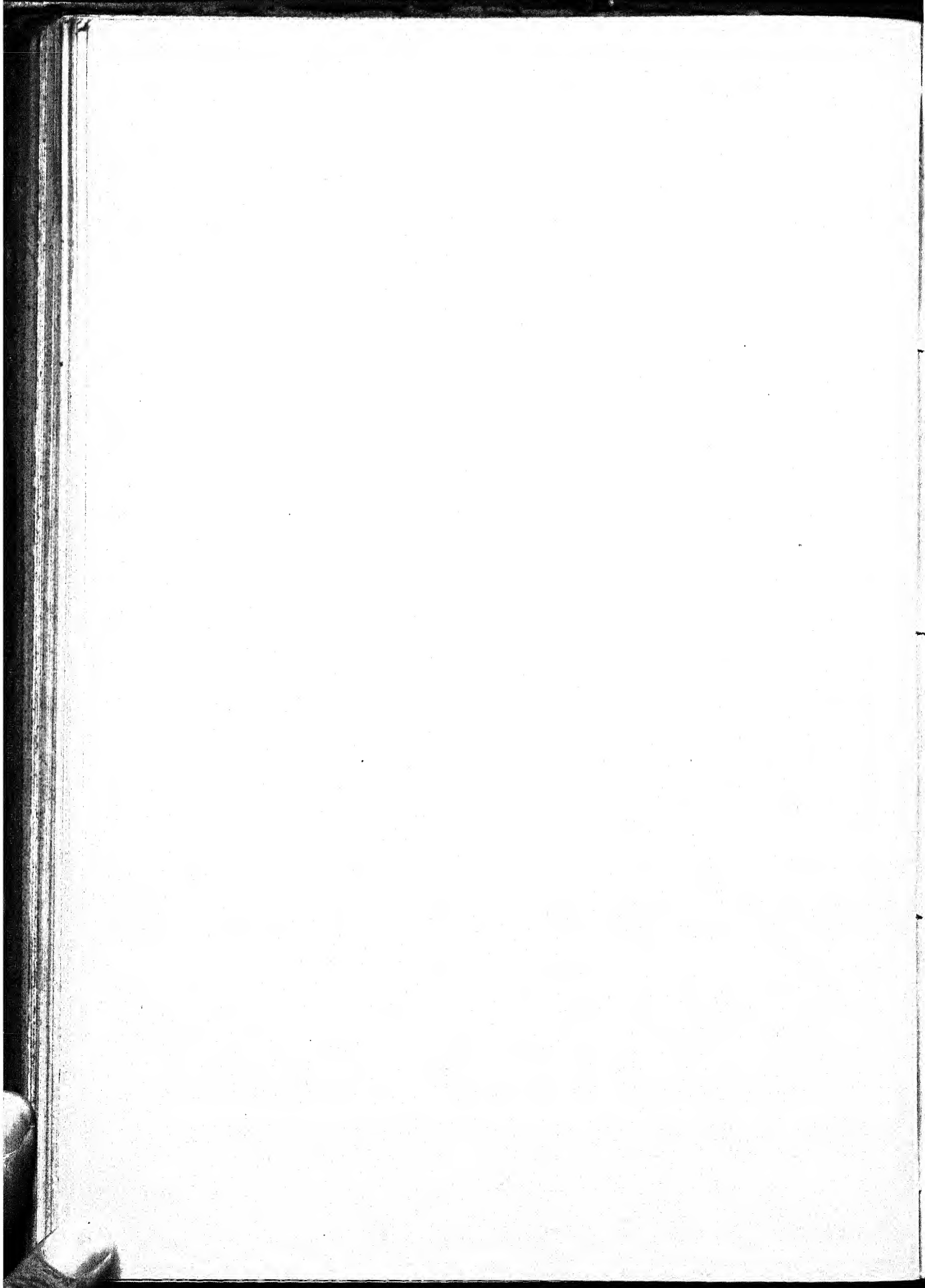
Samples of grass and corn silage and hay were taken during the barn feeding period. A comparison of the average analyses of the forage taken from the fields and of hays as barn fed shows a greater proportionate loss of calcium and magnesium to potassium and the need to improve methods of harvesting to preserve more of the nutrients.

Fourteen ratios of chemical elements in crops, and also the range in ratios between these differentials in composition for each field, are shown. The ratios between the sum of the monovalent sodium and potassium and the sum of the divalent magnesium and calcium are given to implement a reference that milk fever and grass tetany may be associated with an imbalance between these elements.

The roughage grown on this experimental laboratory farm is considered representative of that grown under methods of intensive grassland farming. On this farm there was about the same range in constituents of the forage as that found on more than 150 farms from which samples have been obtained. The wide differences between the composition in the several types of roughage grown on this farm during one season suggest the advisability of having such a variety of long feeds for the complementary insurance afforded.

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# EXTRACTION OF COPPER FROM SOIL AS AFFECTED BY SOLUBLE COMPONENTS OF OAT STRAW AND ALFALFA MEAL<sup>1</sup>

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Copper is recognized as one of the essential microelements for higher plants. Extensive studies have been made of the availability and fixation of soil copper. Soils high in organic matter and acid sandy soils are those most often mentioned in connection with copper deficiency in plants (12).

Copper is present in the soil in the form of neutral insoluble salts (phosphates, sulfides, hydroxides, carbonates), as adsorbed ions on the exchange complex, and in the form of metallo-organic complexes (1). Available copper has been determined, with variable results, by leaching with neutral normal ammonium acetate, sodium chloride, hydrochloric acid, and other replacing solutions. Peech (9) recommended the use of normal sodium chloride solution instead of normal neutral ammonium acetate because of the greater solubility of neutral copper salts in the presence of ammonium ions. Jamison (3) found that *N* HCl removes less copper than do NaCl-HCl or BaCl<sub>2</sub>-HCl solutions, and that acetate is more effective than chloride in the solution of copper from soil.

Fixation of added copper in soil has been found to be affected by pH value and the presence of phosphates, sulfides, and organic matter. Copper is fixed at comparatively low pH values and may be rendered nonexchangeable and unavailable by overliming (10). Moderate amounts of superphosphate increase the solubility of copper in Norfolk fine sand (4,5). Where sulfide ions are present in the soil, the formation of insoluble copper sulfide is to be expected (7). King (6) found an inverse correlation between the amount of organic matter in soil and the solubility of copper applied as bordeaux spray. Jamison (3) expressed the belief that fixation of copper in acid soils must be a result of the formation of slowly soluble organic copper compounds.

The data reported in this paper demonstrate that soluble components of plant residues, commonly added to soil, also influence the solubility of copper in the soil.

## EXPERIMENTAL

Merrimac sandy loam and Dunkirk silty clay loam were used in the following experiments. Merrimac sandy loam is a water-laid soil found extensively in the Connecticut Valley. It is derived from crystalline rock and has good drainage. This particular sample was taken in the fall of 1946 from an experimental plot on the Massachusetts Experiment Station Farm and had been limed to a pH value of 6.7. It had been heavily fertilized and had supported a crop of

<sup>1</sup> Contribution No. 638 from Massachusetts Agricultural Experiment Station, department of bacteriology and public health, Amherst.

potatoes, which necessitated repeated spraying with bordeaux mixture. The sample of Dunkirk silty clay loam<sup>2</sup> was obtained from freshly plowed sod to which nothing had been added for at least 10 years, a cutting of hay having been removed each year. The sample was taken in early spring.

The field moisture was retained in both these soils by keeping the soils in glass jars in the laboratory after they had been passed through a 2-mm. copper screen. Extractable copper was determined by leaching 40.0 gm. (wet weight) of the well-mixed soil with 250 ml. of the designated leaching solution. The leachates were evaporated to dryness, predigested with 5 ml. concentrated  $\text{HNO}_3$ , and digestion was completed with a mixture of 5 ml.  $\text{HNO}_3$  and 5 ml. 60 per cent perchloric acid. The salts were evaporated to dryness with 5 ml. of 1:1 redistilled  $\text{HCl}$  and then dissolved by boiling in dilute, redistilled  $\text{HNO}_3$ . The solution was made to volume, and aliquots were taken for the copper determinations.

The method of copper determination was essentially that described by Drabkin (2). The sample was pipetted into a 60-ml. separatory funnel, 4 ml. of 40 per cent ammonium citrate (purified by dithizone extraction and adjusted to pH 8.5) was added, and the solution made just alkaline to litmus paper with redistilled  $\text{NH}_4\text{OH}$ . Five milliliters of 4 per cent sodium pyrophosphate, 5 ml. of 0.2 per cent sodium diethyldithiocarbamate, and 10.0 ml. of isoamyl acetate were added, and the separatory funnels were shaken for 3 minutes. The isoamyl acetate layer was collected in 15-ml. centrifuge tubes and centrifuged at about 1700 r.p.m. for 5 minutes. The colorimetric measurement was made with a Fisher electrophotometer using the 12-mm. microabsorption cells and a combination filter (Corning 3389 and 5113, one-half standard thickness) having a maximum transmission at 430  $\mu$ . The determinations of 23 standards, each containing 10.0  $\gamma$  of copper, one of which was carried with each set of determinations, were found to have an average variation from the mean of 0.3  $\gamma$  and a maximum variation of 0.8. The precision of the total determination of soluble copper in soil, including sampling and leaching errors, was found to be  $25.1 \pm 1.7$   $\gamma$  Cu per 10.0 gm. dry-weight soil. The maximum variation from the mean of 16 values was 4.1  $\gamma$  Cu.

All reagents, except concentrated nitric and perchloric acids, sodium pyrophosphate, and sodium diethyldithiocarbamate, were purified by redistillation from pyrex glassware or were purified by dithizone extraction (8). Blanks were carried on all reagents and were seldom large enough to necessitate correction.

It was found that the addition of plant residues (oat straw and alfalfa meal) to a soil sample increased the amount of copper extracted from the soil by ammonium acetate leaching solution far more than could be accounted for by the amount of copper added in the residues. Thus, a sample of Merrimac sandy loam, which contained 8.4  $\gamma$  soluble copper in 10.0 gm. dry-weight soil when leached with neutral normal ammonium acetate, was found to yield 22.0  $\gamma$  when oat straw and alfalfa meal were incorporated in the soil at the rate of 200 pounds nitrogen to the acre (C:N = 30:1) prior to leaching. The amount of

<sup>2</sup> Supplied by Kenneth C. Beeson, U. S. Plant, Soil and Nutrition Laboratory, Ithaca, N. Y.

copper added in the plant residues would account for only 1.7  $\gamma$  if the copper in the plant residues were entirely soluble. A similar effect was found when *M* sodium chloride solution was used as the leaching agent, the soluble copper values being 2.3  $\gamma$  for the unamended soil and 20.0  $\gamma$  for the amended soil. The lower value for leachable copper when sodium chloride was used instead of ammonium acetate is due to the greater solvent action of ammonium salts on phosphates and carbonates of copper (9).

Since the increased copper content in the leachate could come only from the soil, it was obvious that addition of the plant residues had resulted in increased solubility of copper in the soil. This was confirmed by steeping an equivalent amount of plant residue in the ammonium acetate, filtering the solution through washed pyrex glass wool, and extracting the unamended soil with this solution. The results were 8.4  $\gamma$  Cu in 10.0 gm. dry-weight Merrimac sandy loam for the unamended soil leached with ammonium acetate, 22.0  $\gamma$  Cu for the amended soil leached with ammonium acetate, and 19.1  $\gamma$  Cu for the unamended soil leached with ammonium acetate containing the soluble material from an equivalent amount of plant residues.

Before the next step was taken, the effect of time of steeping the oat straw and the alfalfa meal in ammonium acetate on subsequent leaching of copper from soil was studied. With the oat straw, 2- and 4-hour steeping showed a slight increase of leachable copper over the 30-minute steeping. With the alfalfa meal, no significant differences in soluble copper between the 30-minute and 4-hour steepings (the two extremes) were found.

The following experiments illustrate the correlation between the amount of soluble components of oat straw and alfalfa meal and the solubility of soil copper. Thirty grams of alfalfa meal was added to 1500 ml. of neutral normal ammonium acetate, steeped for 4 hours with frequent stirring, and then filtered through washed pyrex glass wool. The filtrate was then diluted with neutral normal ammonium acetate to provide a series of dilutions ranging from a filtrate containing the soluble fractions from 5.0 gm. alfalfa meal per 250 ml. ammonium acetate to one containing the soluble fractions from 0.1 gm. per 250 ml. These diluted filtrates (250 ml.) were leached through 40.0 gm. (wet weight) of soil, and the copper in the leachates was determined. The results are given in table 1. The table also shows the results when oat straw replaced alfalfa meal. The reported amounts of copper in the leachates have been corrected for the copper in the filtrates (23.7  $\gamma$  copper in 250 ml. of undiluted alfalfa meal filtrate and 21.2  $\gamma$  copper in 250 ml. of undiluted oat straw filtrate). It is interesting to note that 29.6 per cent of the total copper in the alfalfa meal and 43.7 per cent of the total copper in the oat straw were soluble in ammonium acetate under these conditions, since the total copper contents of the alfalfa meal and oat straw were 83.5 and 48.5  $\gamma$  per 5.00 gm. respectively. The pH value of the neutral *N* ammonium acetate solution was reduced 0.05 unit by the soluble components of 5.0 gm. alfalfa meal in 250 ml. solution.

The question now arises as to what form of copper in the soil is more soluble in the presence of the soluble components of plant residues. The following



experiments indicate that the inorganic, insoluble salts of copper are probably not affected and that the increased solubility of copper comes from the metallo-organic complex.

The differential solubilities of copper sulfide and copper phosphate in neutral normal ammonium acetate solution with and without the soluble components of alfalfa meal were determined as follows: Copper sulfide was prepared by passing  $H_2S$  through a filtered solution of copper acetate. The copper sulfide was then

TABLE 1

*Effect of amount of oat straw and alfalfa meal steeped in ammonium acetate on the leachability of copper from two soils*

PLANT RESIDUE IN 250 ML. NEUTRAL $N$ AMMONIUM ACETATE	COPPER IN 10.0 GM. DRY-WEIGHT SOIL*		
	Alfalfa meal		Oat straw
	Dunkirk silty clay loam	Merrimac sandy loam	Merrimac sandy loam
gm.	$\gamma$	$\gamma$	$\gamma$
0.0	8.4	8.4	8.4
0.1	10.2 $\pm 0.2$	9.8 $\pm 0.2$	9.8
0.25	13.4 $\pm 0.1$	13.9 $\pm 0.2$	11.9 $\pm 0.1$
0.50	17.9	19.5 $\pm 0.8$	16.3 $\pm 0.3$
1.0	31.9 $\pm 1.2$	32.9 $\pm 0.7$	25.3 $\pm 0.2$
2.0	54.7	58.1 $\pm 1.6$	48.5
5.0	89.0	138.1 $\pm 3.8$	121.0 $\pm 1.0$

\* Average of duplicate values and corrected for copper in the leaching solution.

TABLE 2

*Solubility of copper sulfide and copper phosphate in ammonium acetate solution with and without soluble plant residues*

TIME	COPPER AS THE SULFIDE		COPPER AS THE PHOSPHATE	
	No added plant residue	Added plant residue*	No added plant residue	Added plant residue*
days	$\gamma/ml.$	$\gamma/ml.$	$\gamma/ml.$	$\gamma/ml.$
1	75 $\pm 5$	63 $\pm 3$	295 $\pm 5$	278 $\pm 3$
14	204 $\pm 12$	122 $\pm 6$	348 $\pm 3$	350

\* 1 gm. alfalfa meal per 250 ml. solvent. The copper content of the solvent was 0.2  $\gamma$  per ml.

filtered off, washed with a liter of redistilled water, and dried at 37°C. for 4 days. Copper phosphate was prepared by adding a filtered solution of copper acetate to a dilute solution of orthophosphoric acid. The precipitate was filtered, washed, and dried as above. The dried copper sulfide (0.10 gm.) was weighed into each of four 300-cc. Erlenmeyer flasks. To two of the flasks was added 100 ml. of neutral normal ammonium acetate and to the other two was added 100 ml. of the ammonium acetate containing the soluble components of 1 gm. alfalfa meal per 250 ml. solution. The copper phosphate was treated in the same way. The flasks were kept at room temperature with frequent shaking. After 24

hours and after 14 days samples were filtered and copper determinations were made. Copper determinations were also made on the ammonium acetate solution containing the soluble fractions of the alfalfa meal.

The copper values are shown in table 2. This technique is not rigorous but would, nevertheless, reveal the large differences found with soil copper. At 24 hours, no significant differences were observed; after 14 days, copper sulfide showed an appreciably greater solubility in the absence of the soluble components of alfalfa meal. From these results it can be inferred that the inorganic, insoluble salts of copper were not rendered more soluble by the soluble components of the plant residues.

#### DISCUSSION

It is noteworthy that the alfalfa meal seems to contain more of the soluble components per unit weight than does the oat straw. When the amount of copper extracted from Merrimac sandy loam by ammonium acetate solution containing the soluble components of oat straw and alfalfa meal (see table 1) is used, and a stoichiometric proportion of the soluble components to the amount of copper extracted is assumed, the oat straw is calculated to contain about 84 per cent as much of the material as does the alfalfa meal. The close agreement of all but the highest values between the two soils when alfalfa meal is used (table 1) is also noteworthy. Apparently the copper in these soils of differing origin, texture, and treatment reacts in the same way to the solvent action of the soluble plant residues until the reacting copper becomes depleted.

This work indicates a dynamic relationship of availability and fixation of soil copper in the metallo-organic complex. It is possible that in spring and fall, when crop residues are most plentiful in the soil and when soil moisture is highest, soil copper may become more soluble and possibly take part in exchange reactions to replenish the available copper reserves in the soil. Before this thesis can be accepted, however, the availability of this copper to plants and the occurrence of the exchange reactions must be demonstrated.

This solubility effect may also explain Peech's observation (10) that although copper is more firmly fixed in soil than is zinc, copper deficiencies are easily overcome in soil whereas zinc-deficient plants do not readily respond to applications of zinc salts. It is interesting to note that it has been reported that the copper contents of tree leaves are highest in spring and in fall (11).

#### SUMMARY

Soluble components of alfalfa meal and oat straw increased the amount of copper leached from Merrimac sandy loam and Dunkirk silty clay loam by neutral normal ammonium acetate and by *M* sodium chloride solutions. The alfalfa meal appeared to contain about 16 per cent more of this substance than the oat straw, and the amount of copper leached from the soil was directly proportional to the amount of plant residue used. This effect was not found with copper sulfide or copper phosphate. The inference is drawn that the copper in the metallo-organic complex in the soil is the form affected and that the replenish-

ment of available soil copper may be due to increased solubility of copper in spring and fall when plant residues are returned to the soil.

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## THE GENESIS OF LATERITE

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Laterites have been observed and described throughout the history of man's travels in the tropics. Yet research in the lateritic processes of soil formation is still in its infancy. The prevailing confusion in regard to tropical soils may be partly resolved by a better understanding of the nature and manner of formation of laterite, as it has been defined by Pendleton (7). The term "laterite" is used, as originally defined by Buchanan, to designate "an iron-oxide-rich, indurated, quarryable slag-like or pisolitic illuvial horizon developed in the soil profile." It must be understood that laterite, so defined, occurs only in limited extent in the tropics.

Under conditions of abundant moisture and high temperature in humid equatorial regions a rigorous weathering and transformation of parent material occurs. In the final stages of this process of laterization, a horizon develops in which the oxides of iron are concentrated. It becomes indurated upon exposure. This paper reports field observations and results of microscopical studies of laterite profiles from equatorial islands in the Pacific Ocean. The laboratory studies also include the analysis of laterite samples collected by Pendleton in Siam.

### FIELD OBSERVATIONS OF LATERITE IN NEW GUINEA

The depth of weathering and the stage of decomposition of the mineral constituents are very striking in soils of the humid tropics. Measurements were made in British New Guinea of over 50 feet of "zersatz"<sup>2</sup> upon which rests the red loam profile with more or less developed crusts of iron oxide near the surface. Figure 1 represents a section of typical "zersatz" from Oro Bay, New Guinea. The outline of each individual rock of the parent conglomerate has been preserved in minute detail. The advanced stage of weathering is indicated by the ease with which a knife slices the soil material. When crushed between the fingers, the samples reveal a very high clay content.

Climates of the tropics are divided according to Köppen (4) into two types: tropical rain forest and savanna.

In the tropical rain forests, where the soils remain continuously moist, no good examples of laterite were observed. Remnants of fossil horizons, exceedingly resistant to weathering, were found but were interpreted as originating in an earlier age. Generally, the most advanced stage of lateritic weathering in the rain forests is indicated by the presence of a horizon of concretions. This horizon usually occurs at a depth of 3 to 5 feet, at the upper boundary of the soil that re-

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<sup>2</sup> "Zersatz" introduced and defined by Harrassowitz (2) as rocks which have undergone chemical change but have retained their physical appearance.

mains continuously moist. The upper portions of the profile drain after the daily afternoon rains and permit aeration and oxidation of the precipitated oxides of iron.

The best examples of laterite were observed in areas with climates between humid and arid regions at elevations from 500 to 2,000 feet. They occur almost exclusively on level to gently sloping relief. Figure 2 represents such an area in northeastern New Guinea where there is a constant struggle for dominance between the forest and the grass.

Observations by the author indicate that laterite is generally formed within the zone of intermittent saturation. This of necessity requires seasonal periods of drouth, or at least an unequal distribution of rainfall. Mohr (5) in "The Soils of Equatorial Regions," described example after example of laterite formed under these climatic conditions. He asserts, however, that an intermittently dry climate is not necessary. In the Verbeek Mountains of Celebes, he described a



FIG. 1. SECTION OF WEATHERED CONGLOMERATE FROM A DEPTH OF 15 FEET IN A LATERITE PROFILE, ORO BAY, NEW GUINEA. MAGNIFICATION  $\frac{1}{4} \times$

laterite horizon in a continuously wet, equatorial climate. During September and October his climatic data show significantly less rainfall. Is it not possible during this period for sufficient aeration to occur to the depth of the laterite horizon to permit oxidation and partial dehydration of the precipitated oxides of iron? The possibility of a slight modification of the present climate to include more prolonged periods of drouth should not be overlooked.

#### PROCESS OF LATERIZATION

In the process of laterization the primary minerals and their intermediate secondary products must decompose, the silica must be removed, and consequently the oxides of iron and aluminum are left behind. Hydrated aluminum oxide has long been recognized as a component of some soils formed by lateritic weathering (1). Harrison (3) has said, "The mineral of first and direct formation from the plagioclase feldspars is gibbsite." In the highly alkaline pH range of decomposing plagioclase feldspars, solution and mobility of  $\text{SiO}_2$  are accepted without question. Gibbsite ( $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ ) results from hydrolysis of the alkali aluminate solutions. As the alkalinity of the solutions is reduced a chemical reaction takes place and a transformation occurs from one crystalline form to another. Gibbsite no longer remains as a stable product but changes in the presence of  $\text{SiO}_2$  to kaolinite.



Thin sections of samples of granitic and diabase rock constituents of the weathered conglomerate (fig. 1) were made by using a technique of vacuum impregnation with bakelite. Both weathered granite and diabase samples, when properly dispersed, analyze between 90 and 100 per cent clay. Microscopic examination of the thin sections show the residual material from granite to be essentially kaolinite. Kaolinite "worms" are shown in figure 3. The structure of these vermicular crystals of kaolinite indicate they must have developed in place. Ross and Kerr (9) present definite evidence of authigenic crystallization.

Examination of thin sections of the weathered diabase shows the original structure of the rock. The shapes of the crystals of pyroxene are so well preserved

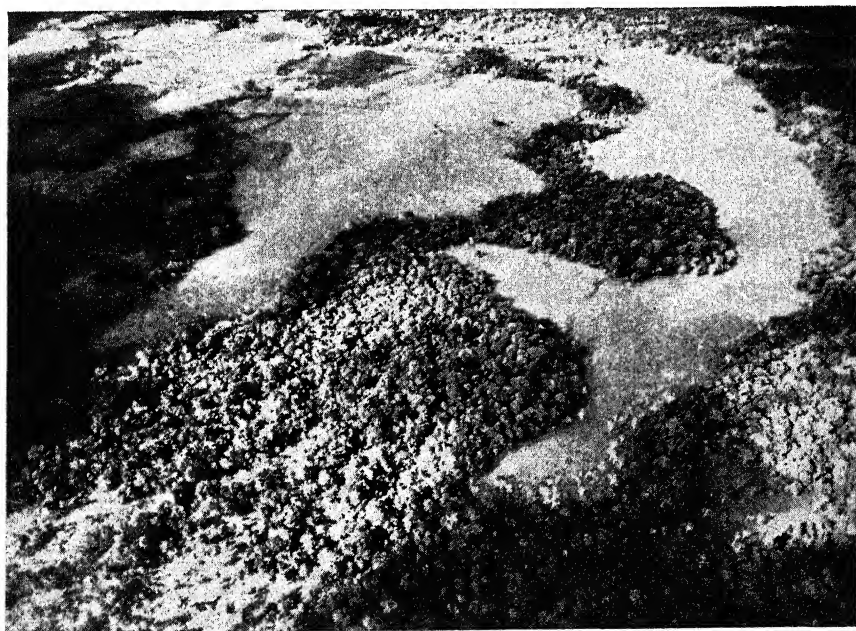


FIG. 2. AREAS OF SAVANNA IN FORESTED REGIONS OF NORTHEASTERN NEW GUINEA

that the angles may be measured, and the laths of plagioclase feldspars are still sharply defined. This preserved structure is shown in figure 4. The preservation of the original structure in the face of nearly complete recrystallization is most interesting. It is difficult to visualize several stages of recrystallization, each with its ensuing volume changes and eventually ending with kaolinite in the original structure. At high magnification the feldspar laths do exhibit a porosity that may explain recrystallization without rupture of original macrostructures. Solution and removal of soluble materials must have progressed far enough to permit the recrystallization with its volume changes.

Alexander and Hendricks (1) report the detection of very small quantities of gibbsite by differential thermal methods. Differential heating curves of prepared mixtures of gibbsite and kaolinite are shown along with curves of the weathered granitic and basic soil material in figure 5. The endothermic peaks at approxi-

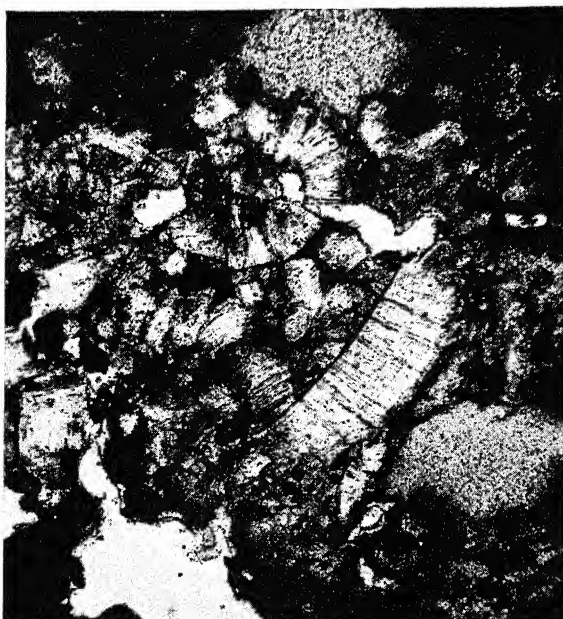


FIG. 3. KAOLINITE WORMS FROM WEATHERED GRANITE, ORO BAY, NEW GUINEA.  
MAGNIFICATION 75 X



FIG. 4. OPHITIC STRUCTURE OF WEATHERED DIABASE CONSTITUENT OF CONGLOMERATE,  
ORO BAY, NEW GUINEA. MAGNIFICATION 50 X

mately 600°C. and the exothermic peaks in the vicinity of 970°C. (not shown) indicate the presence of kaolinite. Thermal analysis shows the weathered granitic soil material to have over 75 per cent kaolinite. The quantities of kaolinite

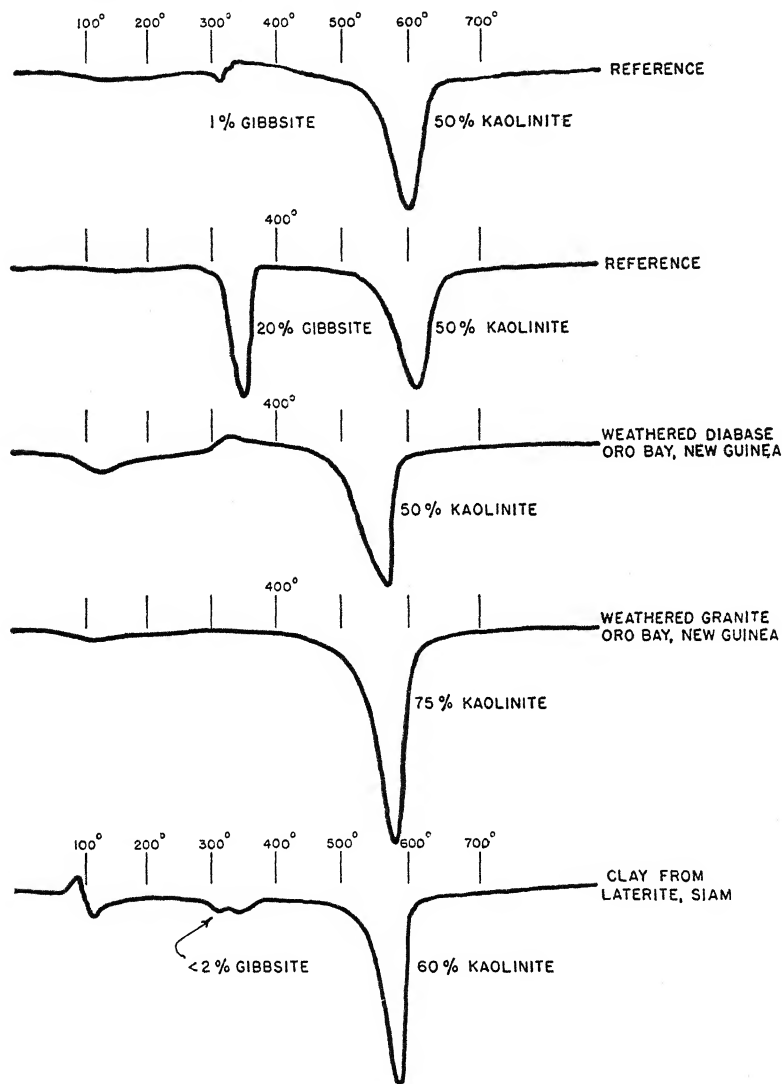


FIG. 5. DIFFERENTIAL HEATING CURVES FOR REFERENCE SUBSTANCES, WEATHERED GRANITE AND DIABASE CONSTITUENTS OF CONGLOMERATE FROM ORO BAY, NEW GUINEA, AND CLAY BETWEEN NODULES OF IRON IN LATERITE FROM CHANTABURI, SOUTHEASTERN SIAM

in the weathered basic material is somewhat lower, 50 per cent, but the absence of appreciable quantities of gibbsite is significant. No observational evidence was obtained to support the presence of gibbsite in an intermediate stage of

weathering. If gibbsite did occur as an alteration product of the plagioclase feldspars, its transformation to kaolinite is complete. In ultrabasic rocks, this cycle occurs in the formation of the clay minerals (1). In moderately basic rocks, sufficient  $\text{SiO}_2$  could be present at the points of recrystallization to effect direct formation of kaolinite without passage through the gibbsite stage.

The thermal curve for the clay between the nodules of iron in laterite from Siam shows essentially kaolinite with a small quantity of gibbsite (<2 per cent). It is apparent that the soil formation process in effect is laterization. It is also apparent that primary laterite, as defined by Harrison (3), will not occur until the clay minerals have been broken by the agents of weathering with release and removal of silica and with accumulation of the oxides of aluminum and iron in their hydrated states. A careful examination of thin sections of these materials shows evidence of solution and decomposition of the secondary silicate minerals and of quartz. The fact that gibbsite occurs only in small quantities indicates that laterization is not in an advanced stage.

#### GENESIS OF LATERITE

Attention in this paper is focused on the origin of the iron crusts. Their position in a representative laterite profile from New Guinea in topographic positions

MATERIAL	THICKNESS
	<i>feet</i>
Red to yellow loam.....	2-6
Iron crust.....	1-5
Zone of concretions.....	3-25
"Zersatz".....	10-80
Fresh rock.....	—

where erosion is not excessive is indicated as follows: Observations of the laterite were made in the field in all stages of formation. Early stages in the formation of iron crusts involve advanced decomposition of the mineral constituents of the parent rock, release and removal of  $\text{SiO}_2$  from the surface horizons, and separation of the sesquioxides.

"Limonite" is used as a generic term to describe the lemon-yellow to brown hydrous iron oxides. It is formed by direct oxidation of iron released in the decomposition of the ferromagnesian minerals. At this point the  $\text{Fe}_2\text{O}_3$  occurs in various degrees of hydration. It orients itself around certain nuclei. It loses water gradually, the rate depending upon the temperature and the pressure of the water vapor in contact with it. Moisture is lost through diffusion in this elastic system. The dehydration follows a smooth curve showing no evidence of the presence of hydrates. X-ray studies (10) of precipitated oxide show the gradual transformation of the yellow to brown gels into crystalline hematite. The color change results from loss of adsorbed water and formation of denser aggregates. A greater specific surface is reflected in the amount of adsorbed water. As dehydration progresses, the surface is reduced, and eventually a compact concretion

is obtained. The iron oxide is dehydrated and irreversibly fixed, primarily during relatively dry periods. Thus the "concretion stage," represented in figure 6, is a definite step in the genesis of laterite.

From a description of the structure of the concretion stage, one recognizes the similarity to Liesegang rings or rhythmic bands of precipitates. Rhythmic banding in gels was first explained by Ostwald (6, p. 778), who assumed supersaturation followed by rapid precipitation. Despite the limitations of Ostwald's theory in its original form, the mechanism which he formulated explains satisfactorily

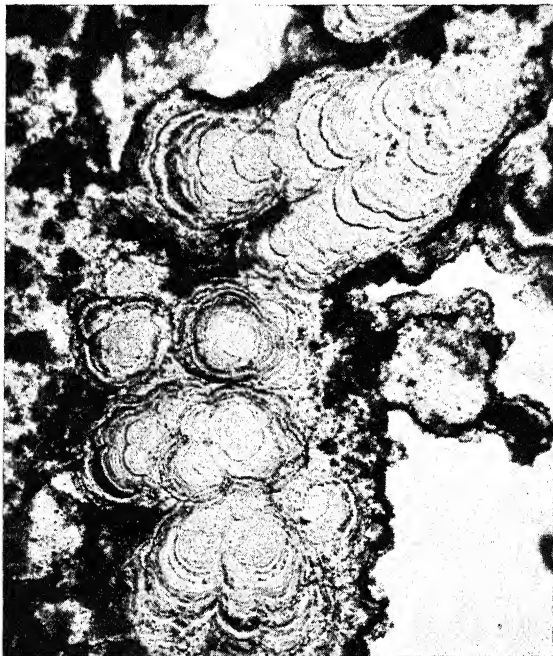


FIG. 6. "CONCRETION STAGE" IN THE FORMATION OF LATERITE. MAGNIFICATION 50 X

most cases of periodic precipitation. Material moves from regions of higher concentration to regions of lower concentration. As the hydrated oxides are precipitated in the vicinity of the concretions, a concentration gradient is established. Iron moves with the gradient and the concretions grow in size as the supply of iron moves into position through voids and channels of the weathering matrix. Figure 7 shows the network of channels through which the hydrated oxides of iron move to the growing concretions.

The growth of concretions and the connecting veins necessarily enmesh many of the crystalline constituents of the matrix. Quartz and secondary silica crystals, showing evidence of solution, and the clay minerals are the principal constituents, with small quantities of the resistant heavy minerals including magnetite, ilmenite, and titanite.

Growth of the concretions continues until an indurated crust is formed. An



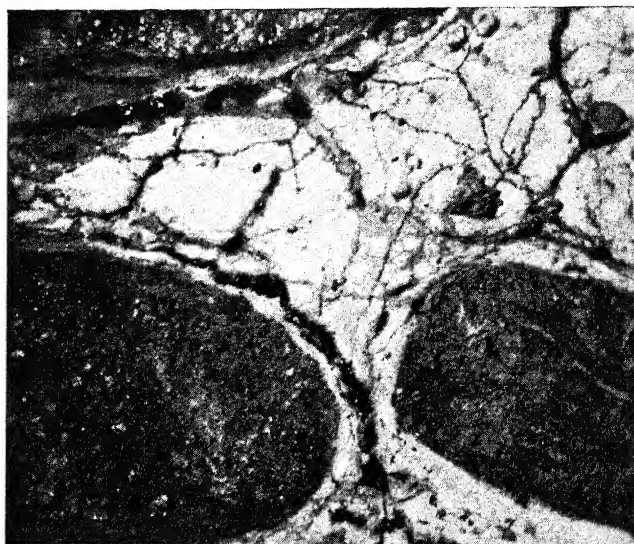


FIG. 7. NETWORK OF CHANNELS CONNECTING CONCRETIONS IN LATERITE FROM CHANTABURI, SIAM. MAGNIFICATION 75 X

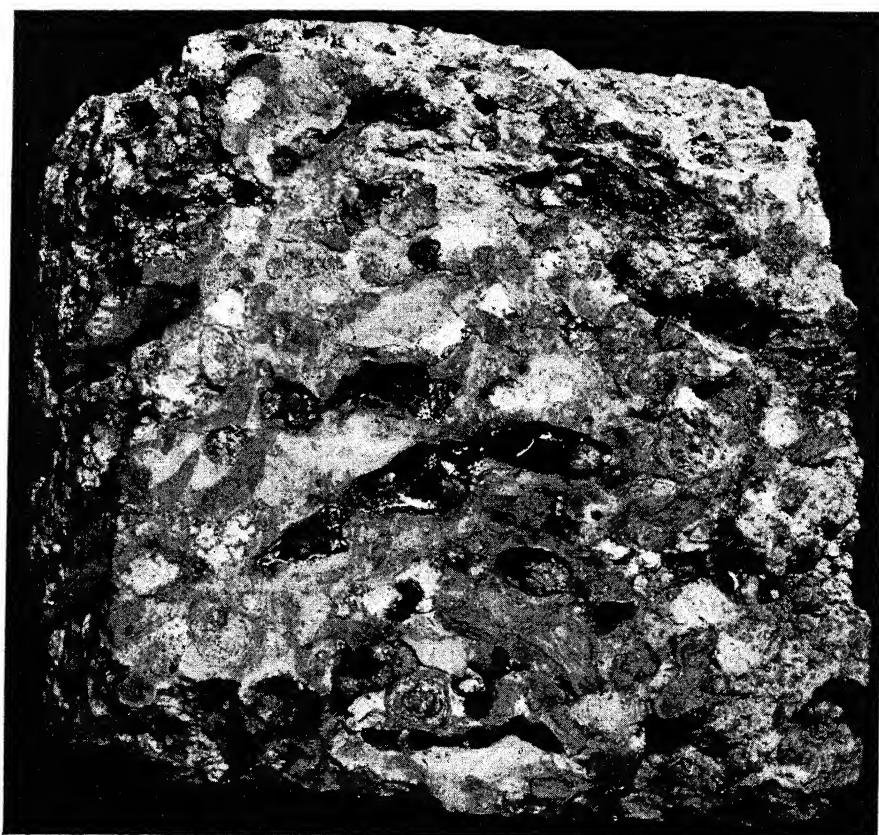


FIG. 8. LATERITE FROM CHANTABURI PROVINCE, SOUTHEASTERN SIAM. MAGNIFICATION 1 X

example of laterite in its advanced stage of formation is illustrated in figure 8. The concretions are cemented together by the oxides of iron. Occasional cavities are filled with clay, the thermal curve of which was presented in figure 5.

Pendleton (8) has divided laterite in two main classes, vesicular and pisolitic, with many intermediate types. The macrostructures of laterite do exhibit variations in form and therefore must be so described and classified. The most striking feature of the pisolitic type is the abundance of globular concretions about the size of a pea. In the vesicular type, one is impressed with its porous nature, its vein-like cementing structures, and a smaller number of concretions. Microstructures of laterite, as shown by petrographic examination, are similar and require no variations in theory of origin. Differences occur primarily in the network of veins that tie the concretions together.

#### SUMMARY AND CONCLUSIONS

The genesis of laterite in New Guinea is presented as an aid to better understanding of tropical soils.

A representative laterite profile from New Guinea is presented with a brief discussion of its weathering and formation. In the tropical rain forests, where the soils remain continuously moist, no good examples of laterite were observed. The most advanced stage of lateritic weathering in the rain forests is indicated by the presence of a horizon of concretions. The best examples of laterite were observed in areas with climates between humid and arid regions at elevations from 500 to 2,000 feet.

Special emphasis is placed on the origin of iron crusts. The genesis of laterite was traced from the nuclei on which the oxides of iron were precipitated, through the "concretion stage," to an indurated horizon. The precipitation, dehydration, and oxidation of iron oxides are discussed in relation to growth of the concretions.

Thin sections prepared by a technique of vacuum impregnation with bakelite made possible studies of structure. The growth of concretions was followed as the iron moved into position through channels of the weathering matrix. The concretions eventually coalesce or become indurated by connecting veins of precipitated oxides of iron.

The classification of macrostructures of laterite by Pendleton (8) is discussed. Microstructures of laterite are similar and require no variations in theory of origin.

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# REGRESSION CURVES OF PLANT GROWTH ON THE LEVELS OF AN ESSENTIAL MICRONUTRIENT

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It is the purpose of this note to describe certain quantitative relationships between plant growth and nutrient levels and to suggest a means for simplifying their interpretation. The problem has been discussed by many writers from the times of Liebig and Sachs. It has been shown that increases in plant growth resulting from addition of a nutrient compound lie on a logarithmic curve which can usually be expressed by a simple mathematical equation (3, 7).

This note presents a method for calculating the responses of growth to the sub-optimal or, at least, subtoxic concentration of the essential micronutrient. Instead of plotting the responses on ordinates against the log of dosages on abscissas, Austin (1), Rissik (6), and others have suggested that the sum total of the cumulated responses be taken as 100 per cent, and that each successive cumulated response in the series be expressed in terms of cumulated percentages. These values, when plotted on the normal probability scale, yield a straight line for "log-normal" distributions, and thus make it easy to transform the sigmoid curve into a straight line.

Experiments on nutrition commonly include a control culture which receives no addition of the substance under study; yet an undeterminable minimum is always contributed by the seed or from other sources. The sum of the responses tends toward a limiting value. Each intermediate cumulated percentage can be plotted against the corresponding nutrient level. Neither the 100 per cent value nor the zero value can be plotted on the probability scale. If the intermediate points lie on a straight line, the regression line can be extrapolated, however, down to the level of the initial response. This may be assumed to intersect the log scale at a level corresponding to the amount of the nutrient under study which was originally present in the medium, as an impurity, or in the seed of the plant.

Data from an experiment on the relation of zinc to the growth of peas will illustrate the use of the regression curve (table 1; fig. 1). The logs of the zinc concentrations were plotted as ordinates and the cumulated percentages for the variants, extending from about 10 to 90 per cent, were plotted on the normal probability scale as the abscissas.

It can be seen that the cumulated percentages of dry weights of tops, 8, 18, 31, 50, 67, and 80, corresponding respectively to 0.005, 0.01, 0.02, 0.05, 0.1, and 0.2 p.p.m., fall on a straight line whether the probability scale is taken as the ordinate or the abscissa. Instead of using log-probability paper we find it more expedient to use the graphical calculator acting as a compound slide rule whereby the cumulated percentages can be plotted on the normal probability scale against any convenient scale of logarithmic cycles affixed on a moveable arm.

TABLE 1

*Relation of zinc concentration to growth and seed production of Dwarf Telephone peas in nutrient solutions\**

ZINC	DRY WEIGHT WHEN HARVESTED				CUMULATED PERCENTAGES OF DRY WEIGHTS			
	Tops	Pods	Roots	Seeds	Tops	Pods	Roots	Seeds
<i>p.p.m.</i>	<i>gm.</i>	<i>gm.</i>	<i>gm.</i>	<i>gm.</i>				
0.000	3.16	0.00	1.21	0.00	2.4		2.5	
0.005	8.40	0.50	2.75	0.00	8.2	1.5	8.1	
0.010	12.12	0.92	5.32	0.26	18.0	4.25	18.5	
0.020	19.38	2.72	8.07	0.85	31	12.42	35	1.4
0.050	24.92	7.80	9.16	12.38	50	35	53	17
0.100	25.78	9.58	8.53	21.27	67	66	71	44
0.200	19.38	6.00	6.65	14.85	80	82	84	75
0.500	21.38	5.66	6.42	21.14				
Totals.....	134.34	33.18	48.11	80.75				

\* From Reed (4).

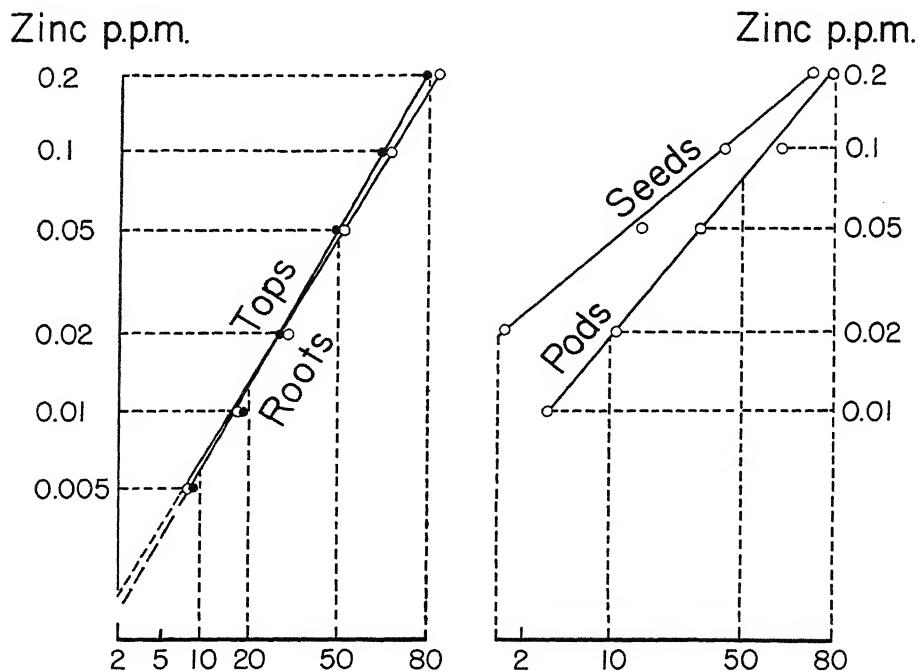


FIG. 1. REGRESSION LINES FOR GROWTH OF PEAS IN NUTRIENT SOLUTIONS DIFFERING ONLY IN THEIR ZINC CONTENTS

In the left hand figure the open circles represent the cumulated percentages for roots; the solid black circles, those for tops.

The regression lines for tops and roots closely approximate each other (fig. 1). The extrapolation of either line cuts the abscissa scale at 2.4 or 2.5 at the level of 0.002 p.p.m. or less of zinc on the ordinate scale. It may be assumed, therefore,



that 0.002 p.p.m. corresponds closely to the amount of zinc carried in the seeds from which the plants grew.

Plotting the points for the seeds and pods makes it possible to draw the regression lines for response to the several dosages. The data in table 1 show that the response of tops and roots differed from that of pods and seeds at corresponding levels of zinc. Since a certain amount of that element was used for the functions of the vegetative system, before any appreciable amount was transferred to pods and seeds, the response, as shown by the slopes of the lines, was bound to be slower.

The same type of statistical analysis can also be utilized to study responses to dosages of an anion, as illustrated by data on the effects of boron on growth of certain plants (table 2). The cumulated percentages for 5  $\gamma$  per 100 cc. (0.05 p.p.m.) are closely related and average 36 per cent; the cumulated percentages for 10  $\gamma$  per 100 cc. (0.10 p.p.m.) are even more closely related and average 64.5 per cent.

Plotting the cumulated percentages (fig. 2) on the probability scale against the corresponding levels of boron added, and tracing lines through the points corresponding to the levels of 5 and 10  $\gamma$  per 100 cc., we obtained regression lines for tops and roots of radishes and of sunflowers (fig. 2). Since the curves are apparently linear, one should be able to predict (if the extrapolation is not carried too far) the amount of boron required to give a 30 per cent yield of these plants. Where special tissues are involved, extrapolation of these types of curves must be avoided. For example, we have already noted the abrupt change in the slopes of the curves for seeds and pods in figure 1 at and above the threshold level for seed production. It seems possible that the same method could be used for studying the relations of auxins to growth.

Anions of auxins are being recognized as links in a chemical system operating both in cytoplasm and in cell wall. Lundegårdh (2) believes that the dissociation of the auxin molecule regulates the arrangement of pectin or cellulose chain molecules in the cell wall. He studied the growth of root hairs (relatively simple structures) in nutrient solutions, with or without heteroauxin at various pH levels, concluding that "Growth curves at varying pH resemble the dissociation curve of a substance with a pK value about 4.5 to 5.0." He suggested that the substance involved might be an auxin,  $pK = 5.0$ , or the heteroauxin, indol acetic acid,  $pK = 4.75$ .

Cations of auxins may also affect growth, either by their pH effect, through direct antagonism of H ions, or by their  $rH$  effect, *e.g.*, interfering with some mechanism of H transfer, as in the  $HS-SH \rightleftharpoons S-S$  equilibrium, or through the formation of a more or less easily dissociable metal complex. Whether the pH or the  $rH$  is involved, the effect of increasing concentrations of any cation in a system may be studied in terms of shift of equilibrium between a complex, incorporating the cation and its binding anion, on the one hand, and either constituent of the complex on the other.

The foregoing discussion is offered as an attempt to rationalize some of our concepts of the growth of plants. We believe that, within limits, it is possible to

determine the relationship between the concentration of a substrate and the response.

TABLE 2  
*Relation of boron concentration to fresh weights of radishes and sunflowers in nutrient solutions\**

BORON PER 100 CC	RADISHES†				SUNFLOWERS‡			
	Tops		Roots		Tops		Roots	
	gm.	per cent§	gm.	per cent§	gm.	per cent§	gm.	per cent§
0	245	9.8	140	17	4.3	4	3.1	11
5	655	36	265	49	29.2	32.5	6.7	36
10	730	65	184	71	29.0	60	7.1	62
50	710	99.5	233	99	40.5	99	10.0	99.5
Totals.....	2340		822		103		26.9	

\* From Reed (5).

† Combined weights of 24 plants.

‡ Average weights per plant.

§ = Cumulated percentages.

Boron p.p.m.

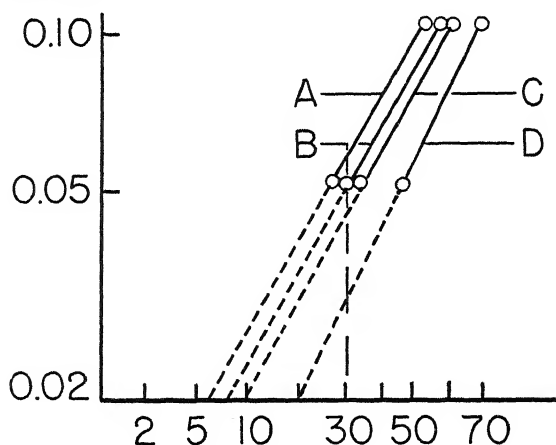


FIG. 2. REGRESSION LINES FOR GROWTH OF SUNFLOWER AND RADISH PLANTS IN NUTRIENT SOLUTIONS DIFFERING IN AMOUNTS OF BORON RECEIVED A, sunflower tops; B, sunflower roots; C, radish tops; D, radish roots.

The technique of expressing the relationships of growth and the concentrations of an essential substrate is simple, yet it has many useful applications.

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## PHOSPHORUS-SUPPLYING POWERS OF 20 NEW JERSEY SOILS<sup>1</sup>

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Part of the soil P is present in mineral form, primarily apatite, and part in an adsorbed or fixed state. This latter P may have had its origin in the soil apatite or it may have been derived from phosphate that was added in fertilizer or manure.

The results of a study of the P-fixing capacities of some important New Jersey soils were presented in a recent paper from this station.<sup>2</sup> The work here reported has to do with the capacities of these same soils to yield both native and applied P to alfalfa plants that were grown on them.

The methods employed were similar to those used in studies of the K-supplying powers of these soils.<sup>3</sup> The general procedure was that of subjecting unphosphated and phosphated A-horizon samples of 20 soils to the continuous action of the roots of alfalfa plants and then determining the amounts of  $P_2O_5$  in the produce of eight successive harvests and, finally, in the roots of these plants.

### OUTLINE OF EXPERIMENT

Supplies of the soils were passed through a 4-mesh screen in preparation for their use in the greenhouse study. Two-gallon solid-bottom pots were employed as containers. Each pot received 13 pounds of soil, except Lakewood and Sassafra sands, of which 15 pounds was used. The volumes of soil in all pots were equalized by addition of washed stones.

Pulverized dolomitic limestone was applied to all soils at the rate of 2 tons per acre.<sup>4</sup> Each pot of soil received K at the rate of 400 pounds  $K_2O$ , half in the form of KCl and half as  $K_2SO_4$ . In addition, salts of B, Cu, Zn, Fe, and Mn were added at rates chemically equivalent to 40 pounds borax. Except for the limestone and phosphate, the materials were divided into eight equal lots, one of which was applied at the start and another after each successive harvest.

The experimental variable was P. To one set of pots no phosphate was added. To a second set, P was applied at the uniform rate of 200 pounds  $P_2O_5$  per acre, which is referred to hereafter as the "standard" rate. To a third set, it was added in amounts that were related to the P-fixing capacities of the soils as they came from the field; this is called the "fixation" rate. The fixation rate of application to Sassafra sand and loamy sand and to Lakewood sand was equivalent to 100

<sup>1</sup> Journal Series paper of the New Jersey Agricultural Experiment Station, Rutgers University, department of soils.

<sup>2</sup> Toth, S. J., and Bear, F. E. Phosphorus-adsorbing capacities of some New Jersey soils. *Soil Sci.* 64: 199-211. 1947.

<sup>3</sup> Bear, F. E., Prince, A. L., and Malcolm, J. L. The potassium-supplying powers of 20 New Jersey soils. *Soil Sci.* 58: 139-149. 1944.

<sup>4</sup> "Acre" refers to 2,000,000 pounds soil.



pounds  $P_2O_5$  per acre, to Merrimac and Lansdale soils 800 pounds, to the Penn soil 1600 pounds, and to the remaining 14 soils 400 pounds.<sup>5</sup>

The phosphate was supplied in the form of  $H_3PO_4$ . This and the starting portions of the other fertilizer materials were dissolved in distilled water and so applied as to allow thorough mixing with the soil. Each lot of soil was then placed in its pot and water was added to optimum moisture content, which was set at 50 per cent of the moisture-holding capacity as determined by the Hilgard method.

As in the earlier work on the K-supplying powers of these same soils, alfalfa was chosen as the experimental plant because it is a vigorous perennial that thrives under greenhouse conditions and collects its own N. Twenty-four seeds of the Ranger variety were planted in each pot on September 12, 1945. The seedlings were gradually thinned until four uniform plants remained on November 1.

The moisture content of the soil was maintained at as constant a level as possible by the daily addition of uniform amounts of water and by weekly weighings. At the weighing periods the pots were rotated on the benches to equalize the light and other environmental factors.

Successive crops were harvested February 7, March 29, May 2, May 29, June 27, July 22, August 19, and September 30, 1946. The produce was dried, weighed, and milled for analysis. At the end of the test the alfalfa roots were screened from the soil, washed, dried, weighed, and prepared for analysis.

#### RESULTS AND THEIR INTERPRETATION

Analytical data on P relationships in these 20 soils are shown in table 1. The total  $P_2O_5$  content varied between 0.01 per cent, in Lakewood sand, and 0.25 per cent, in Hagerstown loam, the average being 0.12 per cent. The P-fixing capacities averaged 31.2 m.e. per 100 gm. soil. They ranged between 0.03 m.e., for Lakewood sand, and 87.5 m.e., for Penn silt loam, at field pH values, and between 0.01 m.e. and 31.5 m.e., respectively, after the soils had been limed to a pH value of 6.5. Liming reduced the average P-fixing capacity 67 per cent.

At the start of this experiment the amounts of extractable  $P_2O_5$ <sup>6</sup> in the unphosphated soils varied between 6 pounds per acre, in Gloucester loam, to over 64 pounds in the Fox and Merrimac soils. After eight harvests of alfalfa without the use of additional phosphate they were considerably reduced in all but eight soils. When phosphate was applied at the standard rate, the amount of extractable  $P_2O_5$  remaining after eight harvests was usually inversely related to the original P-fixing capacity of the soil. This indicates that tests of the P-fixing

<sup>5</sup> At the time these amounts were being decided upon, the P-fixing capacities of several of these soils had not been determined and estimates had to be made. When the fixation data were later obtained, it was found that Chester loam should have received 800 pounds  $P_2O_5$  per acre and Gloucester loam 1,600 pounds instead of the 400 pounds that was applied to each of them.

<sup>6</sup> Peech, M. and English, L. Rapid microchemical soil tests. *Soil Sci.* 57: 167-195. 1944.

capacities of soils provide a fairly reliable index to their relative needs for phosphate.

In table 2 the soils are arranged in accordance with their crop-producing powers without the supplemental use of phosphate. If the limiting factor in the set re-

TABLE 1

*Total and available  $P_2O_5$  in 20 New Jersey soils and the P-fixing capacities of these soils*

SOIL TYPE*	TOTAL $P_2O_5$	P-FIXING CAPACITY†		$P_2O_5$ EXTRACTED BY PEECH METHOD‡			
		At Field pH	At 6.5 pH	Start of Test	End of Test $P_2O_5$ Treatment		
					None§	200¶	F
	%	m.e.	m.e.	lbs.	lbs.	lbs.	lbs.
Collington loam.....	0.19	36.2	17.7	11.9	10.1	14.7	23.6
Lansdale loam.....	0.12	56.5	14.0	11.0	6.4	6.4	16.7
Dutchess shale loam....	0.20	17.1	15.5	21.8	15.3	22.2	21.8
Bermudian silt loam....	0.11	15.3	7.2	20.6	19.5	24.5	36.6
Hagerstown loam.....	0.25	21.1	14.3	14.4	9.6	13.1	20.6
Hoosic gravelly loam....	0.14	12.3	6.4	24.0	11.5	15.6	29.1
Fox gravelly loam.....	0.18	8.2	5.9	64.1	38.9	56.1	80.2
Sassafras loam.....	0.15	18.2	4.9	23.4	17.6	27.0	27.5
Gloucester loam.....	0.18	76.2	16.8	6.0	6.6	11.7	14.7
Dover loam.....	0.12	10.7	4.7	10.1	8.5	12.6	17.6
Whippany silty clay loam.....	0.06	55.8	5.2	20.2	10.3	23.6	26.8
Penn silt loam.....	0.10	87.5	31.5	8.7	8.5	12.8	34.4
Merrimac silt loam.....	0.13	58.8	14.8	64.1	38.5	57.3	112.2
Papakating stony loam..	0.12	34.4	7.9	15.8	9.4	13.3	24.0
Sassafras sand.....	0.02	0.14	0.14	28.6	15.1	35.0	23.6
Chester loam.....	0.12	51.2	15.0	14.2	10.1	11.0	19.5
Washington loam.....	0.04	31.4	11.8	8.0	8.0	11.9	13.7
Lakewood sand.....	0.01	0.03	0.01	32.5	14.7	44.7	30.5
Colts Neck sandy loam...	0.14	24.0	8.8	6.9	7.3	9.2	11.9
Sassafras loamy sand....	0.04	10.1	4.3	10.1	7.6	8.7	10.1

\* In this and all succeeding tables the soils are arranged in order of productivity without added  $P_2O_5$  (see table 2).

† In m.e. per 100 gm. soil. To obtain fixing capacity in soils in terms of tons of 20 per cent superphosphate, multiply m.e. by 1.42.

‡ In pounds per 2,000,000 pounds soil.

§ No  $P_2O_5$  added.

¶ 200 lbs.  $P_2O_5$  per acre added to all soils.

||  $P_2O_5$  applied in accordance with their P-fixing powers as follows: 1,600 lbs.  $P_2O_5$  to Penn silt loam; 800 lbs. to Merrimac silt loam and Lansdale loam; 100 lbs. to Sassafras and Lakewood sands and to Sassafras loamy sand; and 400 lbs. to each of the remaining soils.

ceiving no phosphate is assumed to be a lack of this element, as it was designed to be, the highest-yielding soil on the basis of its total content of  $P_2O_5$  should have been Hagerstown loam, which ranks fifth. This illustrates the fact that no definite relationship existed between the total amounts of native P in these soils and those that were available to the alfalfa plants grown on them.

Comparison of crop yields from the unphosphated soils (table 2) with amounts of  $P_2O_5$  that could be extracted from them at the start of the experiment (table 1) shows little correlation. Thus, Collington and Lansdale loams, with only about 11 pounds extractable  $P_2O_5$  per acre, produced the largest crop yields. This indicates that adequate amounts of soluble  $P_2O_5$  were maintained in these two soils in the unphosphated state to meet the needs for high yields of alfalfa. The Fox

TABLE 2  
*Effect of phosphate applications on alfalfa yields—eight harvests*

SOIL SERIES*	DRY WEIGHT TOPS			DRY WEIGHT ROOTS			INCREASE IN YIELD OF TOPS OVER NO P <sub>2</sub> O <sub>5</sub>		
	P <sub>2</sub> O <sub>5</sub> added†								
	None	200	F	None	200	F	200	F	Average 200 and F
	gm.	gm.	gm.	gm.	gm.	gm.	per cent	per cent	per cent
Collington (4).....	62.6	59.7	59.6	24.5	20.0	21.5	-4.6	-4.8	-4.7
Lansdale (8).....	62.6	81.7	98.0	15.0	21.0	23.0	30.5	56.5	43.5
Dutchess (4).....	61.7	54.7	70.9	21.5	24.5	26.0	-11.3	14.9	1.8
Bermudian (4).....	61.0	60.5	64.0	19.5	30.0	20.0	-0.8	4.9	2.0
Hagerstown (4).....	57.6	66.2	75.0	19.0	25.0	17.0	14.9	30.2	22.5
Hoosic (4).....	56.5	71.4	71.3	19.0	24.0	18.0	26.4	26.2	26.1
Fox (4).....	54.7	56.8	59.4	19.0	19.0	18.0	3.8	8.6	6.2
Sassafras l. (4).....	52.8	64.8	61.9	17.0	19.5	16.0	22.7	17.2	20.0
Gloucester (4).....	52.3	54.1	50.3	17.0	13.0	11.0	3.4	-3.8	-0.2
Dover (4).....	50.6	61.6	66.1	16.0	20.0	18.0	21.7	30.6	26.2
Whippany (4).....	47.1	65.7	71.0	16.0	15.5	20.0	39.5	50.7	45.1
Penn (16).....	46.4	69.1	74.4	14.5	25.0	25.0	48.9	60.3	54.6
Merrimac (8).....	45.0	43.4	52.0	17.0	15.0	18.0	-3.6	15.6	6.0
Papakating (4).....	45.0	55.2	70.3	15.0	20.0	22.0	22.7	56.2	39.5
Sassafras s. (1).....	45.0	51.4	50.1	13.0	23.0	22.0	14.2	11.3	12.8
Chester (4).....	44.4	64.8	56.4	18.0	21.0	20.0	45.9	27.0	36.5
Washington (4).....	41.4	51.3	55.5	16.0	15.0	20.0	23.9	34.1	29.0
Lakewood (1).....	36.2	53.2	50.3	11.0	20.0	14.0	47.0	39.0	43.0
Colts Neck (4).....	33.1	35.0	51.9	13.5	13.0	16.0	5.7	56.8	31.2
Sassafras l. s. (1).....	32.8	41.7	31.3	12.0	16.5	9.0	27.1	-4.6	11.2
Average.....	49.4	58.1	62.0	16.7	20.0	18.7	18.9	26.3	22.6

\* The figure in parentheses after each soil indicates hundreds of pounds  $P_2O_5$  per acre applied under F.

† See footnotes || and ¶ table 1 for explanation of 200 and F.

and Merrimac soils, with 64 pounds of extractable  $P_2O_5$ , ranked seventh and thirteenth in crop-producing powers.

The alfalfa growing on certain of the soils of relatively high P-fixing capacity, such as Collington, Gloucester, and Merrimac loams, did not show significant responses to the use of phosphate. On certain other soils of high P-fixing capacity, such as Penn, Lansdale, Whippany, and Chester loams, very marked increases in yield were produced by its use. This suggests that yield-limiting factors other

than a lack of P had been eliminated to a greater degree from the second group of soils than from the first. Soils of low P-fixing capacity, such as Sassafras and Lakewood sands, required supplemental phosphate for production of even moderately high yields.

The crop increases resulting from using phosphate at the standard rate varied between -11.3 per cent and 48.9 per cent. The effects were negative on Dutchess<sup>7</sup> and Collington loams and on Bermudian and Merrimac silt loams. Very little response was observed on the Fox, Gloucester, and Colts Neck soils. The greatest increase in yield, 48.9 per cent, was obtained on Penn silt loam. The average increase was 18.9 per cent.

When the amount of phosphate applied was adjusted, usually upward, to the fixation rate, further increases in yield resulted. The highest increase, more than 60 per cent, was obtained from the Penn soil, on which the rate of application had been stepped up to the equivalent of 1,600 pounds  $P_2O_5$  per acre. The average increase in yield was 26.3 per cent.

After consideration of yield increases from both rates of application of phosphate, the soils were arranged in order of what was believed to be their relative need for P. This order, beginning with the one in greatest need, is as follows:

*Grouping of 20 New Jersey soils in relation to their phosphorus needs*

(Same soils but not in same order as shown in tables)

GREATEST	MARKED	MODERATE	LEAST
Penn	Chester	Hagerstown	Merrimac
Whippany	Colts Neck	Sassafras l.	Bermudian
Lansdale	Washington	Sassafras s.	Dutchess
Lakewood	Dover	Sassafras l. s.	Gloucester
Papakating	Hoosic	Fox	Collington

The Penn soil stood at the top of the list in P-fixing power. Effects of applied phosphate, whether used at the standard or the fixation rate, were very marked. This soil is thoroughly weathered and contains large amounts of free Fe oxides, which very effectively tie up the added P. Fresh additions of phosphate had, therefore, very marked effects on crops growing on it. In contrast, little effect on plant growth resulted from the use of phosphate on Gloucester loam, a soil of very high P-fixing capacity but one that is much younger and much less weathered than the Penn.

The percentages  $P_2O_5$  in the alfalfa of the second and eighth harvests are shown in table 3. Those in the second crop from the unphosphated Washington, Gloucester, and Dover soils were all 0.422, the lowest in the list. The  $P_2O_5$  content of the second crop from the unphosphated Merrimac soil was 0.682 per cent, the highest in the list. This soil contained more available  $P_2O_5$  than any other at the start of the test but it was thirteenth in the list in crop-producing

<sup>7</sup> The Dutchess, Bermudian, and Fox soils came from areas that had been farmed, whereas all the others were from areas in the virgin state.

power. The average  $P_2O_5$  content of the second crop on the unphosphated soils was 0.512 per cent and that of the eighth crop 0.505 per cent.

When phosphate was applied at the standard rate, the percentage  $P_2O_5$  in the second crop was raised in 19 soils. The range in  $P_2O_5$  content was between 0.514 and 0.812 per cent, the average being 0.646. The average  $P_2O_5$  content of the eighth crop was 0.597 per cent. When phosphate was applied at the fixation

TABLE 3  
*Percentages  $P_2O_5$  in second and eighth harvests of alfalfa tops from 20 soils*

SOIL SERIES*	SECOND HARVEST			EIGHTH HARVEST		
	P <sub>2</sub> O <sub>5</sub> Added†					
	None	200	F	None	200	F
Collington (4).....	.462	.588	.594	.414	.600	.650
Lansdale (8).....	.434	.612	.614	.514	.570	.700
Dutchess (4).....	.532	.632	.688	.682	.750	.744
Bermudian (4).....	.558	.670	.812	.656	.670	.812
Hagerstown (4).....	.570	.682	.762	.570	.526	.752
Hoosic (4).....	.434	.644	.570	.502	.526	.806
Fox (4).....	.520	.768	.936	.608	.756	.960
Sassafras l. (4).....	.588	.744	.594	.788	.730	.918
Gloucester (4).....	.422	.688	.688	.576	.669	.724
Dover (4).....	.422	.588	.614	.440	.538	.738
Whippany (4).....	.482	.546	.608	.366	.582	.706
Penn (16).....	.496	.576	.810	.378	.496	.868
Merrimac (8).....	.682	.780	.868	.564	.688	.818
Papakating (4).....	.520	.638	.490	.428	.606	.644
Sassafras s. (1).....	.614	.612	.490	.744	.724	.644
Chester (4).....	.482	.532	.570	.358	.514	.570
Washington (4).....	.422	.514	.608	.348	.546	.744
Lakewood (1).....	.608	.626	.558	.396	.488	.608
Colts Neck (4).....	.490	.812	.732	.414	.514	.676
Sassafras l. s. (1).....	.508	.676	.806	.354	.464	.606
Average.....	.512	.646	.670	.505	.597	.734

\* See footnote table 2 for explanation of numbers in parentheses.

† See footnote table 1 for explanation of 200 and F.

rate, further  $P_2O_5$  increases occurred in the produce of 15 soils, the average content of the second crop of alfalfa being 0.670 and that of the eighth crop 0.734 per cent.

Composite samples were made of all eight crops on each of the treatments for each soil and these were analyzed for total  $P_2O_5$ . The roots were also analyzed. The data are shown in table 4. The  $P_2O_5$  content was increased following the use of the standard amount of phosphate and still further increased by applications at the generally heavier fixation rate. The differences were much more marked in the roots than in the tops. Thus the  $P_2O_5$  content of the roots averaged 0.357 per cent when no phosphate was applied, 0.619 when the standard



rate was employed, and 0.697 when phosphate was applied at the fixation rate. Root growth was nearly 20 per cent greater in the soils to which phosphate had been applied at the standard rate than in the unphosphated soils and their percentage content of  $P_2O_5$  was nearly doubled. Of the total amount of  $P_2O_5$  contained in the alfalfa about one-fourth to one-fifth was in the roots.

The total amounts of  $P_2O_5$  recovered in all eight crops and in the roots are shown in table 5. The total  $P_2O_5$  in the alfalfa on the unphosphated soils aver-

TABLE 4  
*Percentage  $P_2O_5$  in eight harvests of alfalfa and in roots*

SOIL SERIES*	$P_2O_5$ ADDED†					
	None		200		F	
	Tops	Roots	Tops	Roots	Tops	Roots
Collington (4).....	.496	.328	.670	.706	.726	.658
Lansdale (8).....	.644	.180	.620	.572	.762	.650
Dutchess (4).....	.732	.608	.732	.904	.862	.846
Bermudian (4).....	.718	.632	.744	.620	.864	.608
Hagerstown (4).....	.632	.458	.626	.670	.718	.732
Hoosic (4).....	.514	.292	.626	.526	.886	.686
Fox (4).....	.662	.558	.762	.762	.954	.954
Sassafras l. (4).....	.732	.470	.780	.744	.880	.886
Gloucester (4).....	.562	.266	.682	.470	.762	.632
Dover (4).....	.452	.280	.608	.558	.732	.794
Whippany (4).....	.458	.198	.594	.594	.726	.762
Penn (16).....	.476	.212	.564	.372	.844	.650
Merrimac (8).....	.676	.672	.664	.824	.848	.686
Papakating (4).....	.532	.272	.670	.608	.650	.626
Sassafras s. (1).....	.638	.532	.696	.696	.608	.736
Chester (4).....	.428	.260	.458	.650	.644	.846
Washington (4).....	.464	.198	.614	.818	.756	.632
Lakewood (1).....	.526	.212	.572	.396	.626	.508
Colts Neck (4).....	.462	.292	.658	.446	.706	.644
Sassafras l. s. (1).....	.484	.212	.620	.446	.756	.408
Average.....	.564	.357	.648	.619	.766	.697

\* See footnote table 2 for explanation of numbers in parentheses.

† See footnote table 1 for explanation of 200 and F.

aged 357.7, at the standard rate 498.8, and at the fixation rate 604.7 mgm. These last two values represent increases of 39.4 and 69.4 per cent, respectively.

The differences between the amounts of  $P_2O_5$  contained in the alfalfa that was grown on the unphosphated and the phosphated soils are shown in table 6. As these values indicate the P-recoveries where the standard rate was employed varied between none for the produce of Merrimac silt loam soil and 39.8 per cent for that of Whippany silty clay loam. When the phosphate was applied at the fixation rate, the P-recoveries were between 4.2 per cent for the Merrimac soil and 41.9 per cent for Lakewood sand. On the average, 24.1 per cent of the P

supplied at the standard rate was recovered in the alfalfa and 20.8 per cent of that supplied at the fixation rate. On Penn silt loam, these percentages were 36.8 and 10.9, respectively.

The cation- and P-equivalent values for the composite alfalfa samples from the soils that had received the standard phosphate application are given in table 7. The sums of the cations in terms of milliequivalents per 100 gm. dry tissue closely

TABLE 5  
*Milligrams  $P_2O_5$  in eight harvests of alfalfa and in roots*

SOIL SERIES*	$P_2O_5$ ADDED†								
	None			200			F		
	Tops	Roots	Total	Tops	Roots	Total	Tops	Roots	Total
Collington (4).....	310.5	80.4	390.9	400.0	141.2	541.2	432.7	141.8	574.5
Lansdale (8).....	403.1	39.6	442.7	506.5	120.1	626.6	746.7	149.5	896.2
Dutchess (4).....	451.6	130.7	582.3	400.4	221.5	621.9	611.1	219.9	831.0
Bermudian (4).....	438.0	123.2	561.2	450.1	186.0	636.1	552.9	121.6	674.5
Hagerstown (4).....	364.0	105.3	469.3	414.4	167.5	581.9	538.5	124.4	662.9
Hoosic (4).....	290.4	73.0	363.4	446.9	126.2	573.1	631.7	123.5	755.2
Fox (4).....	362.1	117.2	479.3	432.8	144.8	577.6	566.7	171.7	738.4
Sassafras l. (4).....	386.4	103.4	489.8	505.4	145.1	650.5	544.7	141.7	686.4
Gloucester (4).....	293.9	43.9	337.8	368.9	52.0	420.9	383.3	69.5	452.8
Dover (4).....	228.7	44.8	273.5	374.5	111.8	486.3	379.9	142.9	522.8
Whippany (4).....	215.7	31.7	247.4	390.2	92.1	482.3	515.4	152.4	667.8
Penn (16).....	220.8	44.5	265.3	389.7	93.0	482.7	627.9	162.5	790.4
Merrimac (8).....	304.2	157.9	462.1	288.2	123.6	411.8	440.9	123.5	564.4
Papakating (4).....	239.4	48.9	288.3	369.8	121.6	491.4	456.9	145.8	602.7
Sassafras s. (1).....	287.1	117.0	404.1	357.7	160.0	517.7	304.6	161.9	466.5
Chester (4).....	190.0	46.8	236.8	296.8	136.5	433.3	363.3	169.2	532.5
Washington (4).....	192.1	31.7	223.8	315.0	122.7	437.7	419.6	126.4	546.0
Lakewood (1).....	190.4	53.0	243.4	304.3	79.2	383.5	314.8	71.1	385.9
Colts Neck (4).....	152.9	39.4	192.3	230.3	58.0	288.3	366.4	103.0	469.4
Sassafras l. s. (1)....	158.7	42.4	201.1	258.5	73.6	332.1	236.6	36.7	273.3
Average.....	284.0	73.7	357.7	375.0	123.8	498.8	471.7	133.0	604.7
Average increase (per cent).....						39.4			69.4

\* See footnote table 2 for explanation of numbers in parentheses.

† See footnote table 1 for explanation of 200 and F.

approach a value of 160 from the produce of the 20 soils, which provides further evidence in support of the theory of cation-equivalent constancy within alfalfa.<sup>8</sup> The Ca content of the alfalfa was usually considerably higher than that of Mg. The alfalfa contained almost no Na except for that grown on the Lansdale, Whippany, and Hoosic soils; on these soils the Na content of the alfalfa was about 2 m.e. The Mg contents of the composite alfalfa samples were very similar to

<sup>8</sup> Wallace, Arthur, Toth, S. J., and Bear, F. E. Further evidence on cation-equivalent constancy in alfalfa. *Jour. Amer. Soc. Agron.* 40: 80-87. 1948.

those of P, the average Mg-P ratio being about 1. No correlation could be found between the P-fixing capacities of the 20 soils and the Mg-P ratios within the alfalfa plants grown on them.

TABLE 6  
*Recovery\* of applied  $P_2O_5$ † in eight harvests of alfalfa and in roots*

SOIL SERIES‡	$P_2O_5$ ADDED§							
	200				F			
	Tops	Roots	Total		Tops	Roots	Total	
	mgm.	mgm.	mgm.	%	mgm.	mgm.	mgm.	%
Collington (4).....	89.5	60.8	150.3	25.5	122.2	61.4	183.6	15.3
Lansdale (8).....	103.4	80.5	183.9	31.2	343.6	109.9	453.5	18.9
Dutchess (4).....	-51.2	90.8	39.6	6.7	159.5	89.2	248.7	20.7
Bermudian (4).....	12.1	62.8	74.9	12.7	114.9	-1.6	113.3	9.4
Hagerstown (4).....	50.4	62.2	112.6	19.1	174.5	19.1	193.6	16.1
Hoosic (4).....	156.5	53.2	209.7	35.5	341.3	50.5	391.8	32.7
Fox (4).....	76.7	27.6	98.3	16.7	204.6	54.5	259.1	21.6
Sassafras l. (4).....	119.0	41.7	160.7	27.2	158.3	38.3	196.6	16.4
Gloucester (4).....	75.0	8.1	83.1	14.1	89.4	25.6	115.0	9.6
Dover (4).....	145.8	67.0	212.8	36.1	151.2	98.1	249.3	20.8
Whippany (4).....	174.5	60.4	234.9	39.8	299.7	120.7	420.4	35.0
Penn (16).....	168.9	48.5	217.4	36.8	407.1	118.0	525.1	10.9
Merrimac (8).....	-16.0	-34.3	-50.3	....	136.7	-34.4	102.3	4.2
Papakating (4).....	130.4	72.7	203.1	34.4	217.5	96.9	314.4	26.2
Sassafras s. (1).....	70.6	43.0	113.6	16.7	17.5	44.9	62.4	18.4
Chester (4).....	106.8	89.7	196.5	33.3	173.3	122.4	295.7	24.6
Washington (4).....	122.9	91.0	213.9	36.3	227.5	94.7	322.2	26.9
Lakewood (1).....	113.9	26.2	140.1	20.6	124.4	18.1	142.5	41.9
Colts Neck (4).....	77.4	18.6	96.0	16.3	213.5	63.6	277.1	23.1
Sassafras l. s. (1)....	99.8	31.2	131.0	22.2	77.9	-5.7	72.2	24.1
Average.....				24.1				20.8

\* Obtained by subtracting  $P_2O_5$  content of alfalfa grown on soil to which no P was applied from that of alfalfa grown on P-treated soils.

†590 mgm.  $P_2O_5$  applied per pot in set where P was applied at rate of 200 lbs.  $P_2O_5$  per acre, except for the Sassafras and Lakewood sand in which the application was 680 mg.  $P_2O_5$ . In set where P was applied in amounts related to P-fixing capacities of the soil the amounts of  $P_2O_5$  applied were 300 mg. for the Sassafras loamy sand, 340 mg. for the Sassafras and Lakewood sands, 2400 mg. for the Lansdale and Merrimac soils, 4000 mg. for the Penn, and 1200 mg. for all the remaining soils.

‡ See footnote table 2 for explanation of numbers in parentheses.

§ See footnote table 1 for explanation of 200 and F.

Although the percentage P recoveries were lower when the phosphate was applied at the fixation rate than at the standard rate, the heavier applications usually resulted in the higher yields. It would appear from the data, however, that little is likely to be gained from applying more than 200 pounds  $P_2O_5$  per acre on the sands and 400 pounds on the heavier soil types in preparation for growing alfalfa.

Many peculiarities were noted as to the effects of phosphate applications on alfalfa yields. Yields on the sandier soils of the Sassafras and Lakewood series were markedly improved by applications of 200 pounds  $P_2O_5$  per acre, and they tended to fall off when the rate was reduced to 100 pounds in conformity with the relatively low P-fixing capacity of these soils. Very marked increases were produced on Lansdale silt loam soil both by 200- and 800-pound applications. Marked increases also resulted at both the 200- and 1,600-pound rate on Penn silt loam, but much less crop effect and much lower P recovery were obtained than

TABLE 7  
Cation- and P-equivalent values\* for eight harvests of alfalfa† and the Mg-P ratios within the plants

SOIL SERIES	Ca	Mg	K	Na‡	SUM	P	Mg/P
Collington.....	73	42	45	0.4	160	47	0.89
Lansdale.....	88	47	35	2.2	172	44	1.07
Dutchess.....	84	42	51	0	177	51	0.82
Bermudian.....	71	44	41	0	156	52	0.85
Hagerstown.....	75	51	35	0	161	44	1.16
Hoosic.....	83	42	38	1.7	165	41	1.02
Fox.....	67	57	44	0.4	168	54	1.06
Sassafras l.....	78	49	32	0	159	55	0.89
Gloucester.....	69	49	49	0	167	48	1.02
Dover.....	70	60	38	0	168	43	1.40
Whippany.....	73	49	31	2.2	155	42	1.17
Penn.....	83	42	41	0	166	40	1.05
Merrimac.....	82	39	48	0	169	47	0.83
Papakating.....	85	43	37	0.9	166	47	0.91
Sassafras s.....	51	46	45	0	142	49	0.94
Chester.....	67	42	52	0.4	147	32	1.31
Washington.....	68	47	38	0.4	153	43	1.09
Lakewood.....	53	62	50	0	165	40	1.55
Colts Neck.....	59	38	60	0.4	157	46	0.83
Sassafras l. s.....	72	42	52	0.4	166	44	0.95

\* In m.e. per 100 gm. dry weight of tops.

† From soil receiving 200 lbs.  $P_2O_5$  per acre.

‡ Zeros in this column mean none detectable by method used and indicates that the element is present in amounts less than 0.4 m.e. per 100 gm. dry matter.

on the Lansdale soil. Little increase was effected on the Gloucester soil at either the 200- or the 400-pound rate. Yields on Merrimac silt loam were reduced at the 200-pound rate, and relatively little improvement was effected by raising the rate to 800 pounds.

These studies, taken in conjunction with those dealing with the B, K, and Mg needs of these same soils, show conclusively that each soil represents a distinct problem in itself. Although an attempt was made in each case to equalize all factors other than the one under study, this was not entirely accomplished. Nevertheless, it is evident that these soils differed markedly in their need for

phosphate, in their capacity to fix P, and in their tendency to release both the natural and the applied P to the growing crop.

#### SUMMARY AND CONCLUSIONS

The purpose of this study was to determine the relative needs of 20 important New Jersey soils for phosphate.

The natural  $P_2O_5$  content of the soils varied between 0.02 per cent in Lakewood sand and 0.25 per cent in Hagerstown loam, and it averaged 0.12 per cent.

The P-fixing capacities of these soils in their natural state averaged 31.2 m.e. per 100 gm., varying between 0.03 for Lakewood sand and 87.5 for Penn silt loam, but they were reduced 67 per cent, on the average, by adding pulverized dolomitic limestone to a pH value of 6.5.

The soils were planted to alfalfa, the roots of which were substituted for the laboratory type of extracting agent.

The alfalfa was grown through eight harvests at three phosphate levels: without extra phosphate, at a standard rate of application equivalent to 200 pounds  $P_2O_5$  per acre, and at rates that were related to the P-fixing powers of these soils in their natural state and that varied between 100 and 1,600 pounds.

No correlation was found between the total  $P_2O_5$  content of these soils and their capacity to produce alfalfa without the use of phosphate.

Without added phosphate, the four most productive soils were Collington loam, Lansdale silt loam, Dutchess shale loam, and Bermudian silt loam, and the four least productive were Washington loam, Lakewood sand, Colts Neck sandy loam, and Sassafras loamy sand.

When phosphate was applied at the standard rate the greatest percentage increases in crop yield occurred on Penn silt loam, Lakewood sand, Chester loam, and Whippany silty clay loam.

When phosphate was applied in relation to the P-fixing powers of these soils, the greatest percentage increases in yield occurred on Penn silt loam, Colts Neck sandy loam, Lansdale loam, and Papakating stony loam.

On the basis of both rates of application, Penn silt loam, Whippany silty clay loam, Lansdale loam, Lakewood sand, and Papakating stony loam appeared to have the greatest need for phosphate, and Collington loam, Gloucester loam, Dutchess shale loam, Bermudian silt loam, and Merrimac silt loam the least.

The  $P_2O_5$  content of the alfalfa averaged 39.4 per cent higher on the soils to which P had been applied at the standard rate than on the unphosphated soils, and 69.4 per cent higher on the soils to which it had been applied at the fixation rates.

On the average, 24.1 per cent of the applied P was recovered in the eight successive harvests and in the roots of the alfalfa following the use of phosphate at the standard rate, and 20.8 per cent at the generally much higher fixation rates.

Root development, on the average, was increased nearly 20 per cent by applications of phosphate at the standard rate, and the percentage content of  $P_2O_5$  in the roots was nearly doubled.

The percentage  $P_2O_5$  in the roots of the alfalfa on the phosphated soils was



nearly as high as that in the tops, and the roots contained one-fourth to one-fifth of the total  $P_2O_5$  in the eight harvests and in the roots.

The amounts of extractable  $P_2O_5$  found in the soils at the beginning of the test and after eight harvests of alfalfa were generally inversely related to the original P-fixing capacities of the soils, which indicates that the P-fixing capacity of a soil is a useful guide in determining the amount of phosphate to apply.

With certain soils of relatively high P-fixing capacity, such as Collington, Gloucester, and Merrimac loams, an adequate supply of available  $P_2O_5$  was maintained from the natural reserves of the soil, as indicated by a lack of significant response from the use of supplemental phosphate.

With other soils of high P-fixing capacity, such as Penn, Lansdale, Whippany, and Chester loams, large amounts of supplemental phosphate was essential for maximum crop production.

Soils of low P-fixing capacity, such as Sassafras and Lakewood sands, required supplemental phosphate for maximum yields.

The sums of the cations from composited alfalfa samples from eight harvests, expressed in terms of milliequivalents per 100 gm. dry tissue, closely approached a value of 160, which provides further evidence in support of the theory of cation-equivalent constancy in this plant.

The P- and Mg-equivalent values of the composite alfalfa samples were very similar, the average Mg-P ratio being about 1.

No correlation existed between the P-fixing capacities of the soils and the Mg-P ratios within the alfalfa grown on them.

## MECHANISM OF AGGREGATION OF CLAY MINERALS BY SOLUBLE SILICATES

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Water-soluble sodium silicate was found by Laws and Page (7) to have produced aggregation of certain clay minerals other than the montmorillonitic and also of certain soils.

Dutt (3) observed in a field study that water-soluble potassium silicate markedly increased the stability of aggregates of Dunkirk silt loam which originally had a very poor structure. Moreover, the surface soil of silicate-treated plots had developed a crumb-like structure which persisted in the field for at least 2 months following treatment.

This paper reports the results of a laboratory study of the mechanism of aggregation of clay minerals by soluble silicates.

### METHODS AND MATERIALS

The clay minerals selected for this study were kaolin and bentonite, of the types normally found in mineral soils.<sup>2</sup> The pH values, as determined by glass electrode, were 4.8 for kaolin and 8.9 for bentonite. Kaolin was ground and passed through a 60-mesh sieve before being treated with silicate.

Silicate concentrations<sup>3</sup> equivalent to the amount needed were first diluted with water to a constant volume of 100 ml. and added to 50 gm. of each of the clay minerals. Silicate concentrations higher than those used by Laws and Page (7) were also employed in this experiment. The mixture of clay mineral and potassium silicate solution was thoroughly puddled with a spatula and dried over a steam bath overnight. Kaolin and bentonite, treated with water only and dried in the same way, served as checks.

The aggregating effect of ethyl silicate on kaolin and bentonite was also studied. A 40-ml. portion of 13.8 per cent ethyl silicate solution, prepared in the laboratory, was diluted with 10 ml. of water and added to 20 gm. of each of the clay minerals previously moistened with water. The mixture was thoroughly puddled with a spatula and dried over a steam bath to speed up gel formation. Toward the last stage of drying, the mixture was again puddled and finally dried.

<sup>1</sup> This paper is a part of the research materials of the author's doctorate thesis submitted to Cornell University in 1947. The author acknowledges his gratitude to M. B. Russell and R. Bradfield of Cornell University for their guidance and inspiration.

<sup>2</sup> The kaolin is a product of Ward's Natural Science Establishment, taken from McNamee Mine near Langley, South Carolina; the bentonite, a Wyoming product of the American Colloid Company, Illinois.

<sup>3</sup> Throughout this paper the term "silicate concentration" refers to percentage of anhydrous solid potassium silicate in air-dry clay.

A portion of each clay mineral was treated with alcohol only and dried, to check the effect on aggregation.

Aggregate stability was determined by the wet-sieving technique of McHenry and Russell (8), using materials that passed through a 4.7-mm. sieve but were retained by a 1.98-mm. sieve. The time of shaking was 30 minutes instead of 5 minutes.

Dispersion was determined on the same size-class material as that used in aggregate analysis. Five grams of the material with 200 ml. of distilled water was put into a quarter-liter glass bottle which was kept in a constant temperature bath for 3 hours. The bottle was then shaken end-over-end for 1 minute and transferred to the bath. After 2 minutes, a 10-ml. sample of the suspension was taken at 2 cm. depth, dried at 105°C., and weighed. This weight, expressed in percentage, was taken as the percentage dispersion.

The materials that passed through the 1.98-mm. sieve were ground, passed through a 60-mesh sieve, and stored for pH determination and differential thermal analysis. The pH determination was made by glass electrode in a suspension in which the ratio of clay or clay-silicate mixture to water was 1:40. The suspension was constantly stirred for an hour before its pH was determined.

The relative value of swelling of bentonite, as affected by varying potassium silicate concentration, was determined as follows: 1 gm. of air-dry clay was taken in a graduated 8-ml. vial, 50 by 16 mm., and packed approximately to 1 ml. by gentle jarring. Water was added gently to the top of the clay, and the vial was transferred to a desiccator, which was then evacuated and left in this condition for 24 hours. Excess water was then carefully decanted off, and the interior of the vial was dried with a piece of filter paper. The volume not occupied by the clay and its associated water was determined by filling the vial to the graduated mark with  $\text{CCl}_4$  run gently from a burette. From this value the increase in volume, due to swelling, per gram of clay was calculated.

Differential thermal analysis was run to obtain information on the nature of reaction between clay minerals and soluble silicates. This method has been used by several workers (1, 12) for identification of clay minerals in soils. The samples were brought to moisture equilibrium in an atmosphere of 37 per cent relative humidity prior to thermal analysis. The inert material used was calcined alumina, and the heating rate was 20°C. per minute. In all cases, packing was as uniform as possible, and the amount of material needed to fill the sample hole varied with the kind of material used. Only in the thermal analysis of air-dry potassium silicate was it found necessary to dilute this material with calcined alumina in the proportion of 1:3 in order to facilitate removal of fused potassium silicate. Duplicate determinations were made for each of the samples, and the characteristic features of the curve to be discussed in this paper were exactly reproducible. In determining the reversible or irreversible nature of a certain reaction, the sample under study was treated with water and dried at a temperature slightly higher than that at which the particular reaction occurred. This operation of heating and wetting was repeated three times, after which the sample was put in an atmosphere of 37 per cent relative humidity for moisture-equilibrium. Its thermal curve was then determined.

## RESULTS

*Aggregation, dispersion, and pH*

The data on aggregation, dispersion, and pH of kaolin and bentonite, as affected by varying potassium silicate concentration, are given in table 1. Bentonite shows a decrease, and kaolin shows an increase, in aggregation with increasing potassium silicate concentration from 1 to 10 per cent. At 33.0 per cent silicate concentration and above, aggregation of bentonite again increases, but even at 47 per cent silicate concentration it is still somewhat less than that of the check. It was noticed, during wet-sieving that potassium-silicate-treated bentonite, irrespective of the concentration of silicate used, disintegrated as rapidly as it was

TABLE 1

*Effects of ethyl silicate and of varying concentrations of potassium silicate solutions on aggregation, dispersion, and pH of kaolin and bentonite and on swelling of bentonite\**

POTASSIUM SILICATE CONCENTRATION	KAOLIN			BENTONITE			
	Aggregation	Dispersion	pH	Aggregation	Dispersion	pH	Swelling
<i>per cent</i>	<i>per cent</i>	<i>per cent</i>		<i>per cent</i>	<i>per cent</i>		<i>c.c./gm.</i>
0	12.1	3.8	4.8	73.6	49.3	8.9	3.7
1.0	14.2	9.7	6.8	47.9	51.9	9.0	3.9
3.0	75.2	4.5	9.8	26.2	52.3	9.2	3.8
5.0	79.1	4.0	10.0	1.7	59.9	9.4	3.1
7.0	88.9	3.0	10.0	0.0	68.4	9.5	3.2
10.0	94.6	3.2	10.1	0.0	67.4	9.6	3.2
15.0				0.0	54.0	9.9	2.6
19.0				0.0	49.1	10.0	1.6
33.0				6.1	10.8	10.4	0.2
47.0				66.3	8.6	10.6	0.1
Ethyl silicate.....	96.5	0.9	2.8	40.8	8.3	3.6	...
Alcohol.....	13.4	...	...	71.3	...	...	...

\* All determinations were made in duplicate.

put in water, although a marked decrease in the swelling of bentonite was observed during wet-sieving, particularly at the higher potassium silicate concentration. Wet-sieving does not give a true picture of the aggregation of bentonite when it becomes gelatinous and sticky on being wetted with water.

This observation is also substantiated by the data on the swelling of bentonite (table 1) as affected by different potassium silicate concentrations. These data show that swelling has been greatly reduced at 15 per cent silicate concentration, and has become almost negligible at 33 and 47 per cent silicate concentration. Thus, the rapid disintegration of bentonite at the higher potassium silicate concentration cannot be attributed to the phenomenon of swelling; there must be other factors involved in the process.

There is some anomaly between the results of aggregate analysis and dispersion of bentonite at the higher potassium silicate concentrations (table 1). For

example, though the percentage of aggregation of bentonite at 33 and 47 per cent silicate concentration is apparently less than that of the check, its dispersion is much lower than that of the check and also than that at any other potassium silicate concentration. Dispersion of kaolin, however, has not been affected by potassium silicate treatment, except at 1.0 per cent silicate concentration, where there is some increase in dispersion.

As it is not possible to prepare a sufficiently concentrated sol of alkali-free silica because of a tendency to gel out, ethyl silicate was used to determine the aggregation of kaolin and bentonite by silica sols free from potassium or sodium ions. Ethyl silicate, on hydrolysis, gives ethyl alcohol and silicic acid. On evaporation, ethyl alcohol is expelled, leaving behind the gel of silicic acid, which becomes irreversible on dehydration. Table 1 contains the data on aggregation, dispersion, and pH of kaolin and bentonite as affected by ethyl silicate.

Ethyl silicate has markedly increased the aggregation of kaolin, which is about 96.5 per cent as against 12.1 per cent for the check and which is also slightly higher than that produced by 10 per cent potassium silicate concentration. It is interesting to note that the aggregates formed by ethyl silicate could be easily crushed with fingers in contrast to those formed by potassium silicate, which were hard and compact.

Bentonite, on treatment with ethyl silicate, shows a decrease in aggregation as compared to the check, although its dispersion has been greatly reduced by the same treatment. Air-dry aggregates of ethyl-silicate-treated bentonite disintegrated as soon as they were put in water. In general, the aggregates formed by ethyl silicate behaved toward water in a manner similar to that shown by the aggregates formed by 33 and 47 per cent potassium silicate concentration, except that the former swelled somewhat on wetting. Because of lack of material, no actual measurement on the swelling of ethyl-silicate-treated bentonite could be made.

Results on the binding of loose quartz particles by potassium and ethyl silicate solutions are interesting. It was observed that potassium silicate solution cemented together the loose quartz particles, and the fraction so cemented had stability in water to the extent of about 95.0–96.8 per cent, irrespective of the potassium silicate concentration. Ethyl silicate, on the contrary, separated out as silica gel on treatment and drying with quartz, without any binding or cementation of the quartz particles.

#### *Differential thermal analysis*

In presenting the results of differential thermal analysis, only those features of the thermal curves having bearing on the objective of this experiment are discussed. Because of an initial error in calibration, temperatures at which the reactions of the standard minerals were observed to occur were somewhat lower than temperatures noted by other workers.

The thermal curve of kaolin–10-per-cent-potassium-silicate system (fig. 1, no. 2) does not differ materially from that of pure kaolin (fig. 1, no. 1), whereas the thermal curve of bentonite has been greatly effected by treatment with potas-



sium silicate solution, particularly at the higher concentration (fig. 2). The endothermic reactions between 600 and 700°C. and between 700 and 900°C. show increasing tendency to disappear with increasing potassium silicate concentration,

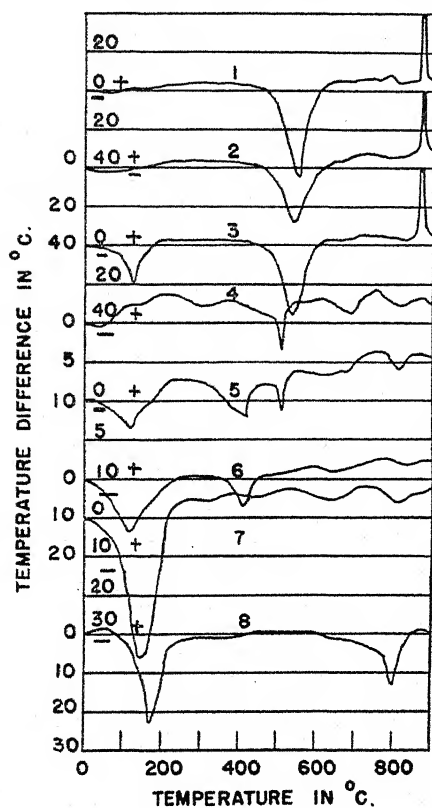


FIG. 1

FIG. 1. THERMAL CURVES OF 1, KAOLIN; 2, KAOLIN-10-per-cent-POTASSIUM-SILICATE SYSTEM; 3, KAOLIN-ETHYL-SILICATE SYSTEM; 4, QUARTZ; 5, QUARTZ-10-PER-CENT-POTASSIUM-SILICATE SYSTEM; 6, POTASSIUM SILICATE; 7, SILICA GEL; AND 8, POTASSIUM CARBONATE

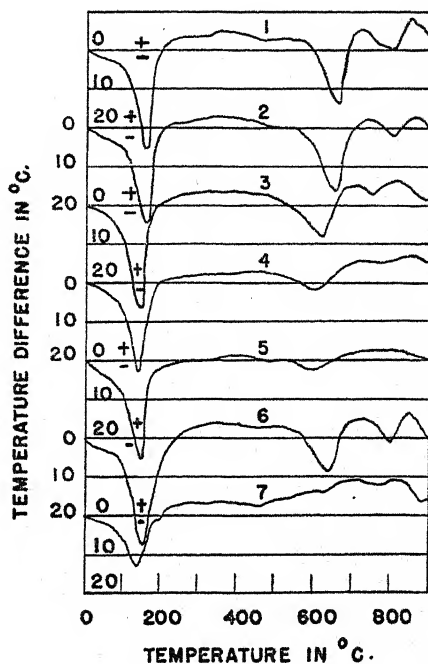


FIG. 2

FIG. 2. THERMAL CURVES OF 1, BENTONITE; 2, BENTONITE-10-PER-CENT-POTASSIUM-SILICATE SYSTEM; 3, BENTONITE-19-PER-CENT-POTASSIUM-SILICATE-SYSTEM; 4, BENTONITE-33-PER-CENT-POTASSIUM-SILICATE SYSTEM; 5, BENTONITE-47-PER-CENT-POTASSIUM-SILICATE SYSTEM; 6, BENTONITE-ETHYL-SILICATE SYSTEM; AND 7, BENTONITE-16-PER-CENT-KOH SYSTEM

while the low-temperature endothermic reaction at about 155°C. and the intensity of this peak are almost unaffected, irrespective of potassium silicate concentration.

The thermal curve of quartz-10-per-cent-potassium-silicate system (fig. 1, no. 5), on the other hand, exhibits, in addition to the endothermic reaction of pure quartz, which occurs at about 510°C. (fig. 1, no. 4), two other endothermic

reactions which are characteristic of potassium silicate (fig. 1, no. 6). The two endothermic reactions of potassium silicate (which was obtained by drying an aliquot sample of potassium silicate solution) at 120°C. and at 420°C. are probably due to the loss of water of constitution. Both of these reactions are irreversible.

Differential thermal analysis was run on silica gel and potassium carbonate to ascertain whether the thermal curve of potassium silicate was that of potassium silicate as such or whether it was also due to silica and potash (which would eventually form  $K_2CO_3$  with  $CO_2$  of the air) which might be liberated by hydrolysis and thus might be present during the subsequent drying of potassium silicate solution. Silica gel was obtained from potassium silicate solution by treatment with HCl and finally washed with water until apparently free from chloride. The endothermic reaction of silica gel (fig. 1, no. 7), which occurs at about 155°C., is due to the loss of surface-adsorbed water and is reversible; the two endothermic reactions of potassium carbonate at 170°C. and at 800°C. are due to the loss of water of crystallization and the decomposition of carbonate, respectively. The thermal reactions of silica gel and potassium carbonate are very sensitive. The presence of these materials even in relatively minute quantities in a mixture can be readily detected by differential thermal analysis unless the mixture contains other constituents with endothermic or exothermic reactions in the same temperature range. In this case there may be an overlapping and masking of the reactions of silica and potassium carbonate.

A comparison of the thermal curve of potassium silicate with that of either silica gel or potassium carbonate does not suggest any separation of silica or potash during the drying of potassium silicate solution. The pH of a 2 per cent suspension of solid potassium silicate obtained by drying was 7.3. It did not differ appreciably from the pH of 2 per cent potassium silicate solution, which was 7.4. Potassium silicate, once it is dried from its solution, seemingly does not again dissolve completely in water at room temperature. The pH measurement, just mentioned, also indicates that there is very little hydrolysis of potassium silicate solution and that there is no appreciable separation of silica and potash during drying. Evidences from other sources (13, 14) also show that hydrolysis of the alkali silicate solution decreases as the concentration of the solution, or the proportion of silica to alkali in the alkali silicate, increases.

The persistence of the endothermic reactions of potassium silicate in the quartz-potassium-silicate system suggests some kind of physical combination between quartz and potassium silicate. The same kind of physical combination, as discussed later, occurs possibly between kaolin and potassium silicate. In that case, the absence of the endothermic reactions of potassium silicate in kaolin-10-per-cent-potassium-silicate system may be attributed to the dilution effect, since in thermal analysis only 0.14 gm. of that system was used as compared to 0.35 gm. of quartz-10-per-cent-potassium-silicate system. But the absence of the reactions of potassium silicate in bentonite treated with as much as 47 per cent potassium silicate concentration cannot be due to dilution effect, since, apart from potassium silicate concentration, which is about five times as high as that used for

treatment with quartz, 0.30 gm. of bentonite-potassium-silicate system was used in thermal analysis.

As is well known, talc and pyrophyllite are structurally similar to bentonite, but they differ from bentonite in having no isomorphous substitution and base exchange and no hydration and swelling. Thermal analysis was run on talc and pyrophyllite each treated and dried with 47 per cent potassium silicate concentration, in order to compare their thermal curve with that of bentonite-47-per-cent-potassium-silicate system.

As shown in figure 3, the endothermic reactions of potassium silicate are readily distinguishable in the thermal curves of talc-and pyrophyllite-potassium-silicate

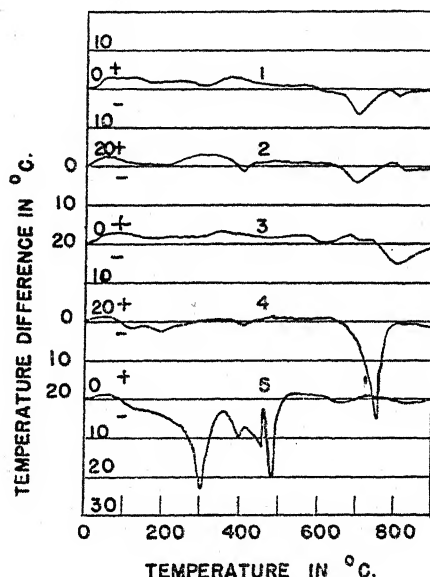


FIG. 3. THERMAL CURVES OF 1, PYROPHYLLITE; 2, PYROPHYLLITE-47-PER-CENT-POTASSIUM SILICATE SYSTEM; 3, TALC; 4, TALC-47-PER-CENT-POTASSIUM-SILICATE SYSTEM; AND 5,  $MgCO_3$

systems, despite the fact that a lesser amount of these materials than of bentonite was used in thermal analysis. Unlike pyrophyllite, talc has undergone radical changes in its thermal character on treatment with potassium silicate: the slight endothermic reaction of talc at 800°C. has completely disappeared and there is, instead, a highly intense endothermic reaction at about 755°C. (fig. 3, no. 4). The fact that the thermal curve of talc-potassium-silicate system differs from that of  $MgCO_3$  (fig. 3, No 5,) excludes the possibility that the endothermic reaction of the former at 755°C. might be due to  $MgCO_3$ , which might be formed from the brucite sheet of talc, if disintegrated by such high potassium silicate concentration, and the  $CO_2$  of the air. An explanation of the two large and two small endothermic reactions in the thermal curve of  $MgCO_3$ , which are due to the decomposition of the carbonate and which are exactly reproducible, is given by

Ephraim (4). Incidentally, the sharp endothermic reaction of talc-potassium-silicate system resembles that of some of the chlorites used by Orcel (11) for thermal analysis. The samples of chlorites from different sources, however, reveal noticeable variations among themselves in their thermal character (6, 11), and whether this particular chlorite-like mineral has been formed prior to or during thermal analysis is a question that can be answered only by further investigation.

Absence of the reactions of potassium silicate in the thermal curve of the system of bentonite-higher-potassium-silicate concentration, as well as suppression of the endothermic reactions of bentonite above 600°C. at the higher potassium silicate concentration, suggests that some kind of chemical reaction involving the alteration of potassium silicate and bentonite might have occurred. Although the hydrolysis of potassium silicate solution, as has been pointed out, is *per se* very slight, it may possibly increase under conditions in which one of the products of hydrolysis is removed by reaction or otherwise. Thus KOH, which is liberated in increasing amounts as it reacts with bentonite and also as the concentration of potassium silicate increases, might have disintegrated this clay mineral especially at the higher potassium silicate concentration. On the other hand, silica, liberated during the same reaction from potassium silicate, tends to maintain the low-temperature endothermic reaction of bentonite below 200°C., as it also has an intense endothermic reaction, which occurred in this experiment at the same temperature as that of bentonite. This hypothesis is supported somewhat by comparison of the thermal curve of bentonite-47-per-cent-potassium-silicate system with that of bentonite treated with 16 per cent KOH, which is equivalent to the amount contained in 47 per cent potassium silicate concentration. The KOH-treated bentonite was dried in a CO<sub>2</sub>-free atmosphere inside a desiccator charged with solid KOH, and then it was transferred to an atmosphere of 37 per cent relative humidity for moisture equilibrium before its thermal curve was determined.

As can be seen from the thermal curve of KOH-treated bentonite (fig. 2, no. 7), all the endothermic reactions of bentonite above 600°C. have completely disappeared whereas its low-temperature endothermic reaction, which is less intense and which occurs at about 140°C.—somewhat lower than that observed for bentonite and bentonite-potassium-silicate systems or silica gel—is probably due to the loss of surface-adsorbed water of the new minerals formed by reaction between bentonite and KOH. The reaction between bentonite and potassium silicate will be less vigorous, however, than that between bentonite and free KOH, and thus the slight endothermic reaction of bentonite between 600 and 700°C. which is present in the thermal curve of the system of bentonite-47-per-cent-potassium-silicate is possibly due to presence of some of the bentonite unattacked by potassium silicate. It is also interesting to note that bentonite developed a yellow color on treatment with either KOH or higher potassium silicate concentration, thus suggesting some similarity in the reaction of these substances with bentonite.

The thermal curve of kaolin-ethyl-silicate system (fig. 1, no. 3) exhibits, in

addition to all the characteristic reactions of kaolin, another endothermic reaction which is very intense and which occurs at about 130°C. Although, because of shortage of material, the thermal curve of silica gel from ethyl silicate could not be determined, it is most probable that this particular reaction of kaolin-ethyl-silicate system is due to silica gel. There is no noticeable difference in the thermal curve of bentonite-ethyl-silicate system (fig. 2, no. 6) and that of pure bentonite (fig. 2, no. 1), except that the low-temperature endothermic reaction of the former below 200°C. is a little more intense, possibly because of the additional loss of water by silica gel.

Caution should be sounded against overestimating the value of differential thermal analysis in soil investigations of the kind reported in this paper. Extreme care and judgment should be exercised in interpretation of the thermal curves, since identification of samples consisting of two or more phases may be confusing if the different phases of the sample have endothermic reactions at nearly the same temperature, if the endothermic and exothermic reactions of the different phases occur in the same temperature range, or if the reactions of some of the phases are not sensitive enough to show up when the phases are present in minute quantities in the samples.

#### DISCUSSION

The question that first poses itself is: What is the mechanism of aggregation between clay minerals and potassium silicate? As is well known, the clay minerals are negatively charged within the ordinary range of soil pH and their electronegative character increases in passing from the acid to the alkaline range. The pH of both kaolin and bentonite increased with increasing potassium silicate concentration (table 1), and with the increasing pH there would be an increase in the electronegative character of both of these minerals (9). Mattson (10) has shown, however, that colloids of the kaolinite type, despite their electronegative character, adsorb silicate ions from sodium silicate solution, whereas those of the montmorillonite type show little or no adsorption of the silicate. It is possible that the low charge of kaolin, which is considered to originate from the dissociation of H ions exposed at the broken edges and faces of this mineral, may not interfere with the adsorption of similarly charged silicate ions, particularly at those points where the intensity of electric field is relatively small or negligible. The cementation of inert quartz by potassium silicate solution also suggests some such adsorption of silicate by kaolin. Moreover, the presence on the surface of kaolin of free oxides of iron may also provide strong linkages for the adsorption of silicates. Once dehydrated, the silicates become irreversible and cement the particles of kaolin into stable aggregates.

With bentonite, however, the relatively high negative charge of this mineral, distributed over its surface uniformly as it is, will tend to retard the adsorption on its surface of similarly charged silicate ions. Moreover, the high-swelling nature of bentonite will also tend to exert a disruptive influence to disintegrate whatever aggregates might have been formed by potassium silicate. According to Arany (2), breaking down of aggregates of alkali soil is not only a simple process



of peptization but is also a function of the swelling pressure of the soil particles, which is great enough to break a glass tube containing the sample. But the fact that the air-dry aggregates of bentonite-potassium-silicate systems, which showed as much swelling as bentonite without silicate, disintegrated more rapidly when put in water, suggests that it is not only the total swelling but also the rate of swelling that is important in such consideration. The rapid breakdown of the air-dry aggregates of bentonite at the higher potassium silicate concentration, at which there was little or no swelling, is not readily explainable. The increase in aggregation of bentonite at 33 and 47 per cent potassium silicate concentration in contrast to the lower potassium silicate concentration is, as the thermal curves suggest, due the fact that the new mineral formed as a result of the breakdown of bentonite by such high potassium silicate concentration, might have crystallized into larger-sized particles and/or might have been aggregated with any excess potassium silicate solution not reacting with bentonite.

The next question that poses itself is: What is the mechanism of aggregation of the clay minerals by ethyl silicate? Gordon (5, pp. 119-121) has shown that silicic acid sols have a definite isoelectric point at about pH 1.217, below which they act as electropositive. It has also been shown by Mattson (9) that the montmorillonite type of clay minerals, although decreasing in electronegative character with decreasing pH, fail to show an isoelectric point within the pH range at which the kaolinite type exhibits an isoelectric point. Both kaolin and bentonite show considerably lowered pH values on treatment with ethyl silicate solution, which must have retained free HCl during its preparation. Thus, the increased aggregation of kaolin by ethyl silicate is most probably due to the mutual coagulation between kaolin and colloidal silica, and the latter on drying becomes irreversible and protects the aggregates against disintegration by water. The reaction between bentonite and ethyl silicate may also be of the same nature; but the lack of an isoelectric point by bentonite makes the effectiveness of coagulation between this clay mineral and silicic acid sols dependent primarily on the reversal of charge by the latter. Moreover, the greater specific surface of bentonite, together with the swelling nature of this mineral, is likely to influence the strength of its bonding with silicic acid.

As mentioned previously, quartz was cemented by potassium silicate solution, though there was no such cementation or binding of quartz by ethyl silicate solution. This contrasting behavior of quartz toward ethyl and potassium silicates suggests that there might be some difference in the aggregating nature of these silicates.

It is logical, then, to conclude that it is the silica fraction of either ethyl or potassium silicate that contributes to the formation of water-stable aggregates, and that the aggregation of the clay minerals by soluble silicates depends on the nature of surface of the former as well as on the nature of silicates. But for silica to be effective as an aggregating agent, it must be present in a soluble condition. The nature and extent of aggregation of different soils by soluble silicates will be a function of the nature as well as of the proportion of the different minerals present.

## SUMMARY

Aggregation of clay minerals, kaolin and bentonite, by soluble silicates and its possible mechanism have been studied.

Kaolin showed an increase in aggregation with increasing potassium silicate concentration: aggregation was greatly increased with 3 per cent concentration and attained its maximum value with 10 per cent concentration, that is, about 94.6 per cent aggregation as against 12.1 per cent aggregation of the check.

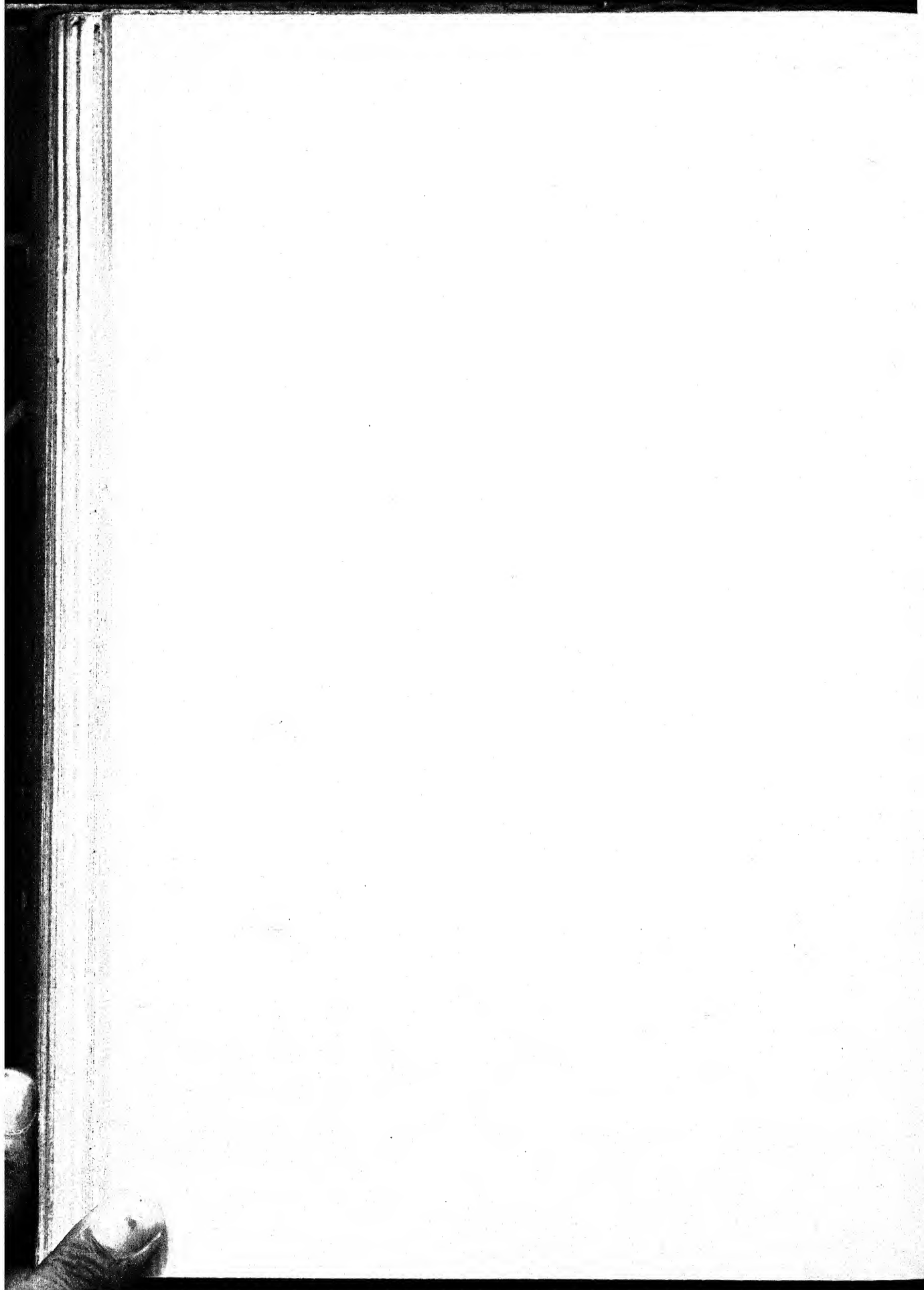
Bentonite, on the contrary, showed a decrease in aggregation within the same range of potassium silicate concentration as was used for kaolin. With further increase in potassium silicate concentration, bentonite showed an increase in aggregation and also a marked decrease in dispersion and swelling.

Ethyl silicate also increased the aggregation of kaolin, which was about 96.5 per cent and slightly higher than that produced by 10 per cent potassium silicate solution. Ethyl silicate, however, decreased the aggregation of bentonite but lowered markedly the dispersion of this mineral.

Differential thermal analysis was used to obtain information on the nature of reaction between clay minerals and soluble silicates. It is the silica fraction of soluble silicates that contributes to the formation of water-stable aggregates, and the aggregation of clay minerals by soluble silicates depends on the nature of silicates as well as on the nature of surface of the clay minerals.

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## DISPARITY IN THE LEACHABILITY OF FLUORINE FROM INCORPORATIONS IN PHOSPHATED AND SLAGGED SOILS<sup>1</sup>

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Until recently the fluorine content of soils was virtually disregarded in analytical procedures. This may be attributed to the fact that the element occurs only in nugatory quantities in soils other than those derived from formations rich in apatite. Moreover, no functional behavior had been attributed to the relatively small quantities of fluorine that reach the soil through incorporations of phosphatic fertilizers and rock phosphate reduction furnace slags or to the meager increments brought by rain waters. Then, too, determination of the minute occurrences of fluorine in soils was not feasible until the titrative technique proposed by Willard and Winter (26) was modified and adapted to that determination (1, 17). The few data on fluorine in soils (5, 25) were augmented substantially, however, though the recent contribution by Robinson and Edgington (24), and several papers have dealt with the fluoride-induced reversions that occur in processed superphosphates and with the possibility that fluoride components of phosphatic fertilizers may induce the reformation of apatite in the soil (7, 10, 11, 12, 14, 23).

Progression in the outgo of fluorine from experimental incorporations cannot be established with certainty through a succession of bulk analyses. The soil systems should not be disrupted through periodic samples, and prescribed acidic distillations may register only fractional fluorine recoveries from the charges of soil. That progression can be determined quickly and with minimum effort, however, through precise determination of the fluorine content of the rain-water leachings obtained by means of the lysimeter. A study of the composition of drainage waters from barium silicofluoride incorporations was inaugurated at the Tennessee Station in 1929 and reported in 1935 (5). Leach and Lipp (3) had recommended incorporation of that fluoride at the rate of 1500 pounds per acre to effect eradication of larvae of Japanese beetles. It appeared advisable to ascertain the fate and effects of the added fluorine, and also to learn whether the barium of the incorporated silicofluoride would pass into sulfate combination and thus cause a critical diminution in the soil's supply of nutrient sulfur. During the third year of a related experiment, lysimeter leachings from variously phosphated soil placements were supplied to Hart, Phillips, and Bohstedt (2) for fluorine analysis, after those workers had concluded that forage crops grown upon phosphated soils did not take up fluorine to a level deemed harmful in livestock

<sup>1</sup> Paper presented before the Division of Fertilizer Chemistry of the American Chemical Society at its annual fall meeting in New York City, September 16, 1947. Some of the findings as to the 6-year outgo of fluorine from slagged soils were obtained through collaboration of J. G. Thompson and George Palmer, of TVA.

feeding. That conclusion was substantiated through the Tennessee Station greenhouse studies, which showed that significant enhancement in fluorine content did not occur in the tops of plants grown on soils that had been enriched in that element far beyond any expectancy from rational incorporations of either phosphatic fertilizers or slags (13). Upon basis of their analyses of the lysimeter leachings supplied by the Tennessee Station, the Wisconsin workers raised the question whether "our present systems of soil fertilization with fluorine-carrying phosphates may lead to a contamination of drinking waters to a point where they may become dangerous to public health" (2). The results here reported may be interpreted as an answer to that query.

The intent of the present contribution is to integrate findings as to the differential leachability of fluorine from distinctive incorporations and the corollary fixation of that element in the three soils of two lysimeter experiments that had different objectives. In both experiments, the incorporations were associated with basic forms of calcium, but the fluorine was retained tenaciously in one experiment and released readily in the other.

#### THE 10-YEAR CALCIUM-FLUORIDE PHOSPHATED SOIL EXPERIMENT

The plan of this lysimeter study called for preparation of a series of soil systems to be enriched equally in phosphorus through single substantial incorporations of calcium phosphates of variant type and "availability." Initially, every phosphate incorporation was to be accompanied by an input of calcium fluoride in excess of the amount requisite for a transition of phosphate to fluorophosphate. The subsequent periodic incorporations of calcium fluoride were to be identical. One objective was to ascertain whether such increments of fluorine would exert identical effect upon the "availability" of tricalcium and dicalcium orthophosphates and calcium metaphosphate after their incorporation into unlimed, limed, and dolomited soils. The rain-water leachings were to be analyzed while the variously phosphated soils were undergoing any effect the added fluorine might exert upon their phosphorus content. The several soils then were to be used in chemical, Neubauer, and pot culture studies to ascertain whether apatite is formed in limed-phosphated soil as it is in limestone-phosphate mixtures (6, 7, 8, 10, 11, 12, 13, 14, 15, 22, 23).

Determinations of fluorine in the rain-water leachings in this study are shown in tables 1 and 2. Each 1/20,000-acre unit designated in these tables represented a 100-pound dry-weight placement of Clarksville silt loam that rested upon a filter bed of quartz in an embedded asphaltum-coated galvanized iron tank, from which the rain-water leachings drained through a blocktin tube into an asphaltum-coated receptacle.

Each of the four phosphatic materials provided a 1,280-pound input of  $P_2O_5$  per 2,000,000 pounds of soil. The limestone, dolomite, and magnesium carbonate were incorporated singly upon basis of 4,000 pounds of  $CaCO_3$ , and only at the beginning of the experiment. The initial pH was 5.46, whereas the final pH values of the limed and dolomited soils were close to 6.2. Every phosphate incorporation, made alone or jointly with a liming material, was accompanied by



TABLE 1

*Fluorine contents of ten annual rain-water leachings from cumulative incorporations of calcium fluoride with various phosphate and limestone and dolomite combinations in Clarksville silt loam*

GROUP	INCORPORATIONS*		OUTGO OF FLUORINE PER 2,000,000 POUNDS OF SOIL											
	Phosphates†	CaF <sub>2</sub>	1936	1937	1938	1939	1940	1941	1942	1943	1944	1945	Total	
		<i>lbs.‡</i>	<i>lbs.</i>	<i>lbs.</i>	<i>lbs.</i>	<i>lbs.</i>	<i>lbs.</i>	<i>lbs.</i>	<i>lbs.</i>	<i>lbs.</i>	<i>lbs.</i>	<i>lbs.</i>	<i>lbs.</i>	<i>per cent§</i>
A¶	None.....	None	0.4	0.4	0.3	0.1	0	0.1	0.2	0.2	0.2	0.3	2.2	...
	Rock phos- phate...	None	0.5	0.4	0.4	0.1	0.2	0.6	0.4	0.5	0.8	0.5	4.5	1.8
	Rock phos- phate and lime- stone  ..	None	0.5	0.6	0.5	0.2	0.8	0.5	0.5	0.6	0.6	0.5	5.3	2.4
	Rock phos- phate dolo- mite....	None	0.6	0.7	0.8	0.3	0.2	0.8	0.7	0.7	1.0	0.4	6.2	3.1
	Rock phos- phate and MgCO <sub>3</sub> ..	None	0.8	1.1	0.7	0.4	0.4	0.6	0.7	0.7	0.9	0.5	6.8	3.6
B¶	Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> ..	None	0.4	0.7	0.5	0	0	0.1	0.2	0.4	0.5	0.3	3.1	...
	Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> and CaF <sub>2</sub> ...	4932	2.5	2.3	3.6	2.4	2.9	6.7	8.2	7.2	10.7	9.4	55.9	2.2

\* Each incorporation was made into full depth of soil. Initial incorporations were made after the soil placements had been subjected to a prefatory 165-day period of leaching by a rainfall of 23.02 inches.

† All phosphate incorporations were at rate of 1,280 pounds of P<sub>2</sub>O<sub>5</sub> per acre, which corresponded to the input provided by the 2-ton incorporation of rock phosphate.

‡ The 1936 incorporation of 328.8 pounds supplied 160 pounds of fluorine; none was added in 1937 and none in 1944; each aggregate of 4,932 pounds of CaF<sub>2</sub> supplied 2,400 pounds of fluorine over the 10-year period.

§ Of the 128 pounds carried by the incorporation of rock phosphate and the 2,400 pounds supplied through CaF<sub>2</sub>.

¶ The materials were incorporated simultaneously.

|| The limestone, dolomite, and MgCO<sub>3</sub> incorporations were at the rate of 4,000 pounds of CaCO<sub>3</sub> per 2,000,000 pounds of soil.

\*\* Limestone incorporation was "aged" 165 days before incorporation of Ca(PO<sub>3</sub>)<sub>2</sub>.

†† The combination was mixed before incorporation into the soil.

TABLE 1—Continued

GROUP	INCORPORATIONS*		OUTGO OF FLUORINE PER 2,000,000 POUNDS OF SOIL											
	Phosphates†	CaF <sub>2</sub>	1936	1937	1938	1939	1940	1941	1942	1943	1944	1945	Total	
		lbs.‡	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	per cent§
C†	Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> , CaF <sub>2</sub> , and lime- stone...	4932	1.5	2.1	4.6	2.8	3.4	7.2	9.4	8.5	13.0	10.0	62.5	2.5
	Ca <sub>2</sub> (PO <sub>4</sub> ) <sub>2</sub> , CaF <sub>2</sub> , and dolo- mite....	4932	1.5	2.1	5.4	3.1	3.8	7.8	9.9	8.5	12.5	9.8	64.4	2.6
	CaHPO <sub>4</sub> ..	None	0.5	0.5	0.2	0.3	0.3	0.2	0.3	0.3	0.6	0.3	3.5	...
	CaHPO <sub>4</sub> and CaF <sub>2</sub> ...	4932	1.6	1.6	3.0	1.6	1.6	4.4	5.3	5.2	8.7	6.7	39.7	1.5
	CaHPO <sub>4</sub> , CaF <sub>2</sub> , and lime- stone...	4932	1.5	1.4	2.9	1.4	1.6	3.9	4.9	4.9	8.6	6.3	37.5	1.4
	CaHPO <sub>4</sub> , CaF <sub>2</sub> , and dolo- mite....	4932	1.5	2.0	3.3	1.5	1.8	4.5	5.7	5.1	9.1	6.6	41.1	1.6
D†	Ca(PO <sub>3</sub> ) <sub>2</sub> .	None	0.5	1.2	0.3	0.3	0.2	0.2	0.3	0.2	0.6	0.3	4.1	...
	Ca(PO <sub>3</sub> ) <sub>2</sub> and CaF <sub>2</sub> ...	4932	2.2	2.1	3.8	2.3	2.4	6.2	7.1	6.0	10.1	8.7	50.9	2.0
	Ca(PO <sub>3</sub> ) <sub>2</sub> , CaF <sub>2</sub> , and lime- stone...	4932	1.4	1.4	2.7	1.5	1.0	3.4	4.6	4.6	8.3	6.1	35.2	1.3
	Ca(PO <sub>3</sub> ) <sub>2</sub> , CaF <sub>2</sub> , and dolo- mite....	4932	1.7	2.0	3.2	1.8	1.6	4.1	5.6	4.9	8.5	6.5	39.9	1.5
E	Ca(PO <sub>3</sub> ) <sub>2</sub> and lime- stone**.	None	1.0	1.1	0.3	0	0.1	0.4	0.5	0.4	0.6	0.4	4.8	...

TABLE 1—*Concluded*

GROUP	INCORPORATIONS*		OUTGO OF FLUORINE PER 2,000,000 POUNDS OF SOIL											
	Phosphates†	CaF <sub>2</sub>	1936	1937	1938	1939	1940	1941	1942	1943	1944	1945	Total	
		<i>lbs.‡</i>	<i>lbs.</i>	<i>lbs.</i>	<i>lbs.</i>	<i>lbs.</i>	<i>lbs.</i>	<i>lbs.</i>	<i>lbs.</i>	<i>lbs.</i>	<i>lbs.</i>	<i>lbs.</i>	<i>lbs.</i>	<i>per cent§</i>
	Ca(PO <sub>3</sub> ) <sub>2</sub> and lime- stone††.	None	0.4	1.4	0.5	0.4	0.1	0.1	0.4	0.5	0.8	0.2	4.8	...
	Ca(PO <sub>3</sub> ) <sub>2</sub> and dolo- mite††..	None	0.4	0.9	0.5	0.3	0.2	0.2	0.5	0.5	0.7	0.4	4.6	...
Rainfall, inches per annum.....			52.11	46.92	64.87	41.28	33.55	48.79	51.89	41.66	55.41	42.88	479.36	...

an initial 160-pound input of fluorine through additions of precipitated calcium fluoride. Additional inputs were withheld until completion of the analyses of the leachings collected during the initial year. The subsequent incorporations of CaF<sub>2</sub> were made at the beginnings of the third year and each succeeding year, other than 1944, and were at the doubled rate of 320 pounds of fluorine per 2,000,000 pounds of soil. Each calcium phosphate incorporation of table 1, therefore, was supplemented by an aggregate per-acre input of 4,932 pounds of CaF<sub>2</sub> that supplied 2,400 pounds of fluorine. Since the initial objectives of the experiment called for identical additions of fluorine to a constant input of P<sub>2</sub>O<sub>5</sub> supplied through variant phosphates, separate incorporations of calcium fluoride were not made.

*Fluorine leachings from inputs of CaF<sub>2</sub> in the phosphated soils*

The findings obtained through periodic determinations were condensed into the 10 annual-period totals shown in table 1. Fluorine outgo from the rock phosphate incorporations was increased invariably, yet slightly, by each jointly added liming material. The mean total for the four rock phosphate units of group A was but 3.5 pounds more than the 2.2-pound outgo from the untreated soil, and represented 2.7 per cent of the quantity carried by the rock phosphate incorporation. The limestone and dolomite incorporations also induced small increases in 29 of the 30 annual leachings of fluorine from the metaphosphate of E group, to which no fluoride was added.

Many of the enhancements in outgo of fluorine were less than 2 pounds per acre per annum during the initial 5-year period, and even after the input had accumulated to 1,120 pounds. Since the 1,100-pound retentions were then some 20 times greater than the potential capacity of a single phosphate incorporation to engender apatite, it is obvious that the retention of the added fluorine was not induced by the phosphates. The fluorine-fixation capacity of the alumino, and

TABLE 2

*Fluorine concentrations in ten annual rain-water leachings from cumulative incorporations of calcium fluoride with various phosphates and limestone and dolomite combinations in Clarksville silt loam*

GROUP	INCORPORATIONS*		FLUORINE FROM 2,000,000 POUNDS OF SOIL										
	Phosphates†	CaF <sub>2</sub>	1936	1937	1938	1939	1940	1941	1942	1943	1944	1945	10-Yr. Mean
		lbs.‡	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.
	None.....	None	0.09	0.08	0.05	0.03	0	0.02	0.04	0.07	0.03	0.06	0.05
A ¶	Rock phosphate.....	None	0.12	0.11	0.07	0.05	0.08	0.02	0.07	0.13	0.12	0.09	0.09
	Rock phosphate and limestone	None	0.09	0.10	0.08	0.06	0.36	0.13	0.09	0.15	0.10	0.09	0.13
	Rock phosphate and dolomite...	None	0.09	0.12	0.09	0.09	0.07	0.17	0.11	0.15	0.13	0.06	0.11
	Rock phosphate and MgCO <sub>3</sub> ....	None	0.15	0.14	0.08	0.11	0.13	0.13	0.11	0.17	0.13	0.08	0.12
B ¶	Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> ....	None	0.08	0.10	0.05	0	0	0.02	0.04	0.09	0.07	0.06	0.05
	Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> and CaF <sub>2</sub> ..	4932	0.21	0.23	0.35	0.68	1.10	1.48	1.44	1.68	1.54	1.62	1.03
	Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> , CaF <sub>2</sub> , and limestone..	4932	0.29	0.36	0.60	0.80	1.24	1.56	1.64	1.99	1.83	1.72	1.20
	Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> , CaF <sub>2</sub> , and dolomite...	4932	0.29	0.43	0.74	0.91	1.45	1.63	1.58	1.97	1.76	1.66	1.24
C ¶	CaHPO <sub>4</sub> .....	None	0.10	0.10	0.03	0.10	0.12	0.04	0.06	0.07	0.08	0.05	0.08
	CaHPO <sub>4</sub> and CaF <sub>2</sub> ..	4932	0.30	0.31	0.41	0.48	0.62	0.96	0.90	1.22	1.25	1.14	0.76
	CaHPO <sub>4</sub> , CaF <sub>2</sub> , and limestone..	4932	0.29	0.29	0.41	0.41	0.59	0.85	0.86	1.13	1.20	1.06	0.71
	CaHPO <sub>4</sub> , CaF <sub>2</sub> , and dolomite...	4932	0.30	0.36	0.41	0.36	0.68	0.94	0.93	1.17	1.22	1.09	0.75
D ¶	Ca(PO <sub>3</sub> ) <sub>2</sub> ....	None	0.09	0.16	0.04	0.10	0.09	0.04	0.05	0.08	0.09	0.05	0.08
	Ca(PO <sub>3</sub> ) <sub>2</sub> and CaF <sub>2</sub> ..	4932	0.41	0.38	0.53	0.64	0.94	1.34	1.21	1.46	1.41	1.41	0.97
	Ca(PO <sub>3</sub> ) <sub>2</sub> , CaF <sub>2</sub> , and limestone..	4932	0.28	0.31	0.37	0.41	0.37	0.75	0.80	1.12	1.16	1.03	0.66
	Ca(PO <sub>3</sub> ) <sub>2</sub> , CaF <sub>2</sub> , and dolomite...	4932	0.34	0.37	0.45	0.50	0.62	0.88	0.92	1.20	1.18	1.09	0.76

\*. †. ‡. ¶. ||. \*\*. †† See corresponding footnotes, table 1.

TABLE 2—*Concluded*

GROUP	INCORPORATIONS*		FLUORINE FROM 2,000,000 POUNDS OF SOIL										
	Phosphates†	CaF <sub>2</sub>	1936	1937	1938	1939	1940	1941	1942	1943	1944	1945	10-Yr. Mean
		lbs.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.
E	Ca(PO <sub>3</sub> ) <sub>2</sub> and lime- stone**....	None	0.18	0.13	0.04	0	0.05	0.10	0.09	0.09	0.08	0.06	0.08
	Ca(PO <sub>3</sub> ) <sub>2</sub> and lime- stone††....	None	0.08	0.17	0.06	0.10	0.03	0.02	0.07	0.12	0.11	0.04	0.08
	Ca(PO <sub>3</sub> ) <sub>2</sub> and dolo- mite††....	None	0.07	0.18	0.07	0.10	0.06	0.03	0.09	0.12	0.10	0.07	0.09
Rainfall, inches per annum.....			52.11	46.92	64.87	41.28	33.55	48.79	51.89	41.66	55.41	42.88	Total 479.36

other soil components may have become satisfied to the extent that the leachings of fluorine were then from the unaltered fluoride.

Fluorine leachings from the tricalcium phosphate, group B, exceeded those from any corresponding joint addition with the dicalcium and metaphosphates in groups C, D, and E. The tricalcium phosphate appeared most conducive to fluoride leachability and, conversely, least fixative toward the added fluorine. Upon examination by the technique proposed for the identification of precipitated tertiary calcium phosphates (18), the additive phosphate of group B was found to be a hydroxy-apatite. It registered a citric acid solubility of 97 per cent, against 76 per cent for its calcine, which attained the x-ray pattern of oxyapatite. The 65-pound outgo of fluorine from the CaF<sub>2</sub> addition with Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> on the dolomited soil was maximal among the 10-year recoveries from the nine units in groups B, C, and D, and represented 2.6 per cent of the 2,400-pound common input.

*Other components in leachings from the fluoride-phosphated soils*

Since the leachings from Clarksville silt loam were subjected to "complete" analysis, each fluorine outgo was compared with its concomitant outgo of calcium. Of the 385-pound increase in the outgo of calcium (CaCO<sub>3</sub>) from the rock phosphate, only 6 pounds could be attributed to the concomitant outgo of fluorine. The increase in calcium outgo from the incorporations of rock phosphate was from carbonate and phosphate combinations, unless the rock phosphate stimulated dissolution of native soil components.

Calcium leachings from the calcium fluoride in combinations with tricalcium phosphate and with calcium metaphosphate were 592 pounds (CaCO<sub>3</sub>) and 433 pounds more than the amounts leached from the respective phosphates alone. Since these two substantial enhancements in calcium outgo were derived from the incorporations of CaF<sub>2</sub>, from which there was a small outgo of fluorine, it is



obvious that the fluorine retention is attributable in part to a selective fixation of the fluorine. The leachings from the dicalcium phosphate incorporations, however, did not indicate like phenomena. The calcium outgo from the joint addition of  $\text{CaHPO}_4$  and  $\text{CaF}_2$  was 32 pounds ( $\text{CaCO}_3$ ) less than that from the  $\text{CaHPO}_4$  alone, whereas the fluorine outgo from that joint addition was equivalent to 95 pounds of  $\text{CaCO}_3$ . This apparent inconsistent behavior of the dicalcium phosphate incorporation is subject to clarification.

The magnesium and potassium contents of the leachings also were determined, although possible influence of the phosphate-fluoride combinations upon the outgo of those elements from their native occurrences in the soil is not a primary consideration in the present paper. In general, the rock phosphate, tricalcium phosphate, and dicalcium phosphate incorporations effected some repression upon the outgo of potassium, and repression was furthered by a supplement of limestone and of dolomite. The rock phosphate may have induced a slight repression upon outgo of magnesium, whereas the tricalcium phosphate incorporation may have induced some enhancement. In general, however, the several phosphatic materials exerted no appreciable effect upon the uniformly small outgo of magnesium.

It is pertinent to note that silica was present only in nugatory quantities in the leachings from the phosphated soils of groups A to E of tables 1 and 2. Such meager quantities were deemed of no effect in the present experiment and hence were not determined quantitatively. In contrast, substantial quantities of solvated silica were carried by the leachings from the two calcium silicate materials used in the companion experiment (see table 5).

*Fluorine concentration in leachings from the  $\text{CaF}_2$ -treated phosphated soils*

Since there was no surface "runoff" of the rain waters that fell within the periphery of the lysimeters, the proportions of rainfall collected as leachings were larger than the proportions that would have become drainage waters in the field. Moreover, the lysimeter leachings passed from the full-depth incorporations directly into the receivers and, therefore, were not subject to retardation and retention by underlying untreated soil or subsoil. Hence, it is probable that the fluorine concentrations shown in table 2 were greater than those that would be encountered in the drainage waters from similar inputs and comparable rainfall in the field.

The leachings from rock phosphate incorporations carried fluoreine in concentrations invariably below 0.14 p.p.m. Every liming supplement served to raise that concentration, but the increases were not appreciable. Obviously, detrimental concentration of fluorine will not occur in the ground waters from soils to which rock phosphate incorporations are made at rates within economic limits.

During the first 4 years of the experiment, the leachings from the phosphate +  $\text{CaF}_2$  groups B, C, and D showed increases in the concentration of fluorine from the 800-pound aggregate of the first three incorporations of  $\text{CaF}_2$ , but all such increases were less than 0.9 p.p.m. After the third year the tertiary phosphate units of group B invariably yielded the highest fluorine concentrations, which

then ranged between 1 p.p.m. and 2 p.p.m. Although the drainage waters from the  $\text{CaHPO}_4 + \text{CaF}_2$  of group C showed progressive increases in fluorine content, a concentration of 1 p.p.m. did not develop until the eighth year. The fluorine input then aggregated nearly 2,000 pounds, such as would be supplied through 200 additions of superphosphate at the rate of 500 pounds per acre.

The limestone and dolomite supplements registered no uniformly significant effect upon the concentration of fluorine in the leachings from the fluoride that was added with  $\text{Ca}_3(\text{PO}_4)_2$  and with  $\text{CaHPO}_4$ , in groups B and C. All of the leachings from the simultaneously added mixtures of metaphosphate with limestone and with dolomite showed higher concentrations of fluorine after the fifth year; but, from the 20 comparisons of group D in table 2, it appears that the limestone and dolomite caused a decrease in the fluorine concentration below that shown by the leachings from the metaphosphate +  $\text{CaF}_2$  control.

The lack of significant distinctions between the concentrations of fluorine in the leachings from groups C and D may be accounted for through assumption that the incorporated metaphosphate underwent hydration to the ortho form and then passed into the dicalcic combination in the limestoned units; the phosphate inputs of groups C and D, therefore, might be rated as duplications.

#### THE 6-YEAR SLAGGED-SOIL EXPERIMENT

The over-all objective of this lysimeter experiment was to determine the behavior, effects, and fate of incorporations of the efficacious fluoride-bearing quenched calcium silicate slag that comes from the electric rock-phosphate-reduction furnaces. A particular objective was to ascertain whether the incidence of fluorine in the drainage waters from slagged soils might reach concentrations that would constitute a health hazard. The academic appeal of the study was augmented by practical considerations. The quenched Wilson Dam slag had been used extensively and satisfactorily in several states as a means of an initial liming that also supplies one effective incorporation of  $\text{P}_2\text{O}_5$  (16). Supplements of phosphates were not prescribed in this experiment, but the slag contained 1.5 per cent of  $\text{P}_2\text{O}_5$ , presumably as a "solid solute" of apatite in calcium silicate.

The "glassy" slag, S-795, of previous experiments, had a neutralization value of 84 per cent  $\text{CaCO}_3$ -equivalence (9, 16). It contained fluorine equivalent to 6.7 per cent of  $\text{CaF}_2$ , although x-ray examination did not yield a pattern indicative of component calcium fluoride. But the pattern of that fluoride was registered when  $\text{CaF}_2$  was contained in a simulative pulverized mixture with amorphous calcium sucate. Since the precipitated  $\text{CaF}_2$  did yield a pattern when diluted to a 7 per cent content in its mixture with the nonpattern sucate, it is concluded that the fluorine content of the slag was not in the simple fluoride form.

The slag was incorporated into Hartsells fine sandy loam, pH 5.0, and into Baxter silt loam, pH 5.2, in three finenesses and at four rates, in parallel with equivalent quantities of limestone of like sizing. The Baxter soil was similar to the Clarksville soil used in the preceding experiment. Although not identical, these two silt loams were of common origin.

The soil placements and equipment were similar to those described for the phosphated soil experiment, as was also the technique of full-depth incorporation and annual remixing. One exception was the handling of the 10 units of series L and M of table 3, which were not disturbed during the 6-year period. To ascertain whether underlying unslagged zones effect substantial retentions of the fluorine carried by the leachings from the slagged zone, inputs of 640 pounds and 1,280 pounds of fluorine per acre surface were supplied through incorporations of 100-mesh slag into the upper half of the soil placements of the four units of M group.

*Fluorine leachings from the incorporations of quenched calcium silicate slag*

The 14 comparisons of table 3 show that limestone-control incorporations invariably caused some increases in the relatively small leachings of fluorine from the contents native to both soils.

Substantial increases in fluorine leachings came from the 20-ton full-depth incorporations of 100-mesh slag in the L group during the initial year. After 6 years, the four largest aggregates were from those 1,280-pound single inputs and from the 1280-pound inputs of group I carried by the four 5-ton incorporations of the 4-mesh slag, which contained 74 per cent of material finer than 20-mesh. The outgo of fluorine from those four incorporations surpassed the outgo from the single 20-ton incorporation of 100-mesh slag in the undisturbed L series in the Hartsells soil. This quantity relationship stands somewhat reversed, however, in a like comparison for the more retentive Baxter silt loam. Significant increases in fluorine outgo came from the single 5-ton incorporations of the "unground," or 4-mesh slag, in both soils during the second year and from the repetitions of the 2-ton incorporations of the 20-mesh and 100-mesh separates. Decreases in particle size of the slag and heavier incorporations were reflected by the corresponding increases in fluorine outgo during the third year and thereafter.

Fluorine leachings from the 20-ton full-depth incorporations of 100-mesh slag in the undisturbed group L of the two soils were about three times those from identical inputs into the upper zone, in group M. Moreover, the fluorine outgo from the 640-pound input into the upper stratum of soil was only a third or less of the outgo from the full-depth inputs of 512 pounds that were supplied by the several 8-ton aggregates of 20-mesh and 100-mesh slag in groups J and K. The sorptive effect of the substratum was registered also by the fact that the outgo of fluorine from each 640-pound single incorporation into the upper stratum soil was less than the outgo from each 320-pound incorporation carried by 5 tons of 4-mesh slag.

*Fluorine concentration in leachings from the incorporations of quenched calcium silicate slag*

The data of table 4 show that almost every incorporation of slag caused an increase beyond 1 p.p.m. of fluorine in the leachings during the initial year. The 20-ton incorporations induced abnormally high concentrations of about 40 p.p.m. of fluorine in the leachings from the soils of group L, and concentrations in the

TABLE 3

Fluorine carried by the drainage waters from incorporations of quenched calcium silicate slag in two soils

GROUP	LIMESTONE, SLAG, AND WOLLASTONITE INCORPORATIONS						* FLUORINE OUTGO, POUNDS PER 2,000,000 POUNDS OF SOIL																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																										
	Materials		Mesh	Quantity tons	Number	Depth	Fluorine lbs.	Hartsells fine sandy loam					Baxter silt loam																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																				
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\* Except for the soils of groups L and M, which were not disturbed during the 6-year period, the soils that received single incorporations were remixed in parallel with those that received repetitive incorporations.

† Incorporations in groups I, J, and K represent the initial incorporation and three annual repetitions.

TABLE 4  
Fluorine concentrations in six annual rainwater leachings from incorporations of quenched calcium silicate slag in two soils

GROUP	LIMESTONE, SLAG, AND WOLLASTONITE INCORPORATIONS							MEAN CONCENTRATION OF FLUORINE IN SOLUTION													
								Hartsells fine sandy loam							Baxter silt loam						
	Materials	Mesh	Quan- tity	Number	Depth	Fluorine		1940	1941	1942	1943	1944	1945	Mean	1940	1941	1942	1943	1944	1945	Mean
			tons			lbs.		p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.
F	None	...	...	...	...	...		0.2	0.4	0.1	0.2	0.4	0.4	0.3	0.2	0.3	0.1	0.1	0.4	0.4	0.3
	Limestone Slag	4 4	5 5	1* 1	Full Full	1 320		0.5 1.6	0.6 13.7	0.3 3.8	0.3 4.5	0.8 4.5	0.4 4.5	0.5 5.4	0.4 1.6	0.6 12.5	0.2 3.2	0.2 3.9	0.8 4.0	0.4 3.5	0.4 4.8
G	Limestone Slag	20 20	2 2	1 1	Full Full	0.4 128		0.3 0.9	0.4 3.1	0.2 0.9	0.2 1.2	0.6 1.4	0.4 0.8	0.4 1.4	0.3 0.8	0.3 2.5	0.1 0.6	0.1 0.8	0.6 1.0	0.4 0.6	0.3 1.1
	Limestone Slag	100 100	2 2	1 1	Full Full	0.4 128		0.3 1.3	0.5 4.0	0.2 1.0	0.2 0.8	0.6 2.6	0.4 0.8	0.4 1.8	0.2 1.2	0.3 2.4	0.2 0.9	0.1 0.9	0.4 1.4	0.4 0.8	0.3 1.3
I	Limestone Slag	4 4	5 5	4† 4	Full Full	4 1280		0.2 1.7	0.7 41.5	0.2 18.8	0.5 25.7	0.6 26.0	0.6 20.0	0.4 22.3	0.4 1.7	0.6 23.0	0.3 10.1	0.3 16.1	0.2 20.0	0.4 14.0	0.4 14.2
	Limestone Slag	20 20	2 2	4 4	Full Full	1.6 512		0.1 0.9	0.6 10.4	0.2 7.0	0.5 15.5	0.6 22.0	0.6 12.0	0.4 11.3	0.2 0.9	0.5 8.0	0.2 5.8	0.2 13.3	1.2 18.0	0.4 10.0	0.5 11.2
K	Limestone Slag	100 100	2 2	4 4	Full Full	1.6 512		0.2 1.1	0.6 14.0	0.2 13.6	0.4 21.0	1.0 22.0	0.6 10.0	0.5 13.6	0.3 0.9	0.6 15.6	0.2 17.3	0.2 23.2	0.6 27.0	0.4 10.1	0.4 15.7
	Limestone Slag Wollastonite	100 100 100	20 20 20	1 1 1	Full Full Full	4 1280 ...		0.4 42.5 0.5	0.6 72.2 1.0	0.2 17.6 0.3	0.3 15.1 0.4	0.8 22.0 1.4	0.6 12.0 1.0	0.5 30.2 0.8	0.3 37.9 0.5	0.6 58.3 0.9	0.2 12.7 0.4	0.2 15.7 0.3	1.4 18.0 0.8	0.4 10.0 0.6	0.5 25.4 0.6
M	Slag Slag	100 100	20 10	1 1	Upper half Upper half	1280 640		0.7 0.8	3.7 4.2	2.5 2.4	3.1 3.3	14.0 5.5	10.0 0.7	5.7 2.8	0.9 1.2	3.4 1.4	1.0 0.5	2.2 0.8	7.0 2.0	8.0 5.5	3.8 1.9
								35.8	55.0	50.0	51.3	49.1	53.7	204.9	35.8	55.0	50.0	51.3	49.1	53.7	204.9
	Rainfall, inches per annum .....													Total							Total

Rainfall, inches per annum .....

\*. † See corresponding footnotes table 3.



range of 11 to 15 p.p.m. were registered by the 512-pound inputs of fluorine carried by the four successive 2-ton incorporations of the 20-mesh and 100-mesh slags.

The undisturbed 20-ton incorporation of 100-mesh slag induced the highest concentrations of fluorine in the 6-year leachings from both soils. Determination of the amounts of  $\text{CaCO}_3$  engendered from those incorporations established the fact that the major fraction of metasilicate of the slag had undergone disintegration during the initial year and that virtually complete disintegration had occurred before the expiration of the second year. Such disintegration is correlated with maximal concentrations of fluorine in the leachings from the slagged soils during the second year. In 14 instances, concentrations then exceeded the 10 p.p.m. attained through a  $\text{CO}_2$ -saturated aqueous extraction of calcium fluoride in the laboratory.

Although the substratum of untreated soil decreased the quantity of fluorine carried by the leachings from the upper-zone incorporations of 10 tons and 20 tons of 100-mesh slag, the diminished concentrations were still substantially beyond the concentration admissible for fluorine in potable water. This comparison is of significance, in that the stoppage effected by the untreated zone of soil in the lysimeters is but a fraction of the retardation that would have been effected by a corresponding stratum of clay subsoil. The capacity of subsoil to absorb percolant solutes and ions is such that the ultimate increase in the fluorine content of the ground waters from slagged soils probably would come slowly and to no great extent.

#### INTEGRATION AND INTERPRETATION OF RESULTS FROM THE TWO EXPERIMENTS

Every liming material induced some increase in every annual rain-water leaching of fluorine from the 2-ton incorporations of rock phosphate. In terms of parts per million in solution and as pounds of fluorine per acre, however, the enhancements were so small as to warrant the conclusion that the fluorine content of the drainage waters from economic incorporations of rock phosphate would not create a health hazard.

The data of tables 1 and 3 show the marked disparity between the meager outgo and corollary near-complete retention of the additive fluorine by the phosphated Clarksville silt loam—unlimed, limed, and dolomited—and the ready release of large quantities of fluorine to the leachings from the slagged Hartsells fine sandy loam and Baxter silt loam. Since the silt loams of the two experiments were from the same mother material, distinction being due chiefly to a difference in chert content, the two soils are deemed virtually identical.

During the initial year, the small enhancements in the outgo of fluorine from the directly added calcium fluoride were, in general, greater than the outgo from the quantities introduced as a component of the slag. The leachings from the 20-ton incorporations of 100-mesh slag in the two soils of L group of table 3 were distinct exceptions. That combination of rate and fineness induced an outgo of fluorine far beyond that from any initial 160-pound input as  $\text{CaF}_2$  and imparted

to the leachings a fluorine concentration twice that listed for a saturated aqueous solution of calcium fluoride.

The leachings from the Hartsells and Baxter soils attained the maximal concentrations of 72 p.p.m. and 68 p.p.m. of fluorine with concomitant enrichment in calcium bicarbonate during the second year. The small leaching of fluorine from the phosphate-fluoride-limestone combinations in the Clarksville soil cannot be attributed, therefore, to repression from an excess of calcium solutes. The subsequent leachings of fluorine from the incorporations of slag were far greater than those from the larger inputs supplied by the multiple annual additions of calcium fluoride. Thus, after 9 years' cumulative residue of some 2,340 pounds of fluorine (from the 4,809-pound equivalence of  $\text{CaF}_2$ ), the leachings of the tenth year carried only 10 pounds of fluorine, in contrast to the 97-pound outgo from the 957-pound residue in the slagged Baxter soil.

Several factors militate against conclusion that the small outgo of fluorine from the phosphated soils is attributable to a repressive effect of the limestone and the dolomite upon the leachability of the incorporated fluoride—(a) that crystalline salt is dissolvable but slightly, even when it is a pulverulent precipitate; (b) the leachings of calcium indicated that a fraction of the incorporated  $\text{CaF}_2$  did not persist as such in the phosphated soils; (c) fluorine leachability was not repressed by the high concentrations of calcium bicarbonate also present in the leachings from the heavy-rate incorporations of slag; (d) incidence of calcium fluoride in the slag is not established; or (e) that the disintegration and sequential carbonation of heavy incorporations of slag effect releases of calcium fluoride to the leachings. Moreover, since the outgo of calcium from every incorporation of slag was greater than that from every corresponding incorporation of limestone, the disparities between small outgo of fluorine from the  $\text{CaF}_2$ -treated soils and large outgo from the slagged soils cannot be explained upon basis of "common ion effect."

The near-complete retention of the fluorine introduced through the successive intimately mixed incorporations of  $\text{CaF}_2$  was effected by the variously phosphated soils in their acidic condition, as well as when they had received moderate incorporations of limestone and of dolomite. Since the leachability of fluorine from the incorporations of  $\text{CaF}_2$  without additive  $\text{PO}_4$  was not an objective initially, and with a limitation in number of lysimeters, separate incorporations of the fluoride were not made. Hence, it is not established that fluorine leachings from the units that received the potentially reactant calcic phosphates and the cumulative inputs of  $\text{CaF}_2$  were materially different from the leachings that would have come from incorporations of fluoride without a calcium phosphate. Moreover, any retention of fluorine attributable to the development of apatite would be a negligible factor, since the 1280-pound single incorporation of  $\text{P}_2\text{O}_5$  in every unit of groups B, C, D, and E of tables 1 and 2 could react with only 58 pounds of the 2,400-pound aggregate input of fluorine. Related findings indicate the probability that the development of aluminofluoric compounds in the acidic and moderately limestoned soils is responsible for the near-complete fixation of the fluorine of the  $\text{CaF}_2$  incorporations.

When the substantial outgo of fluorine from the slagged soils is contrasted with the near-complete retention of fluorine by the phosphated soils, it is essential to recognize a fundamental distinction between the nature and fates of the supplemental calcic incorporations in groups B to E in tables 1 and 2, and those in groups F to M in tables 3 and 4. The incorporation of an excess of limestone into an acidic soil results in the *liberation* of  $\text{CO}_2$  and a residuum of limestone, whereas the disintegration of an equivalent excess of a glassy calcium silicate results in an accumulation of  $\text{CO}_2$  as  $\text{CaCO}_3$  and of hydrated silica. Since the leachings from the phosphated soils carried only meager quantities of  $\text{SiO}_2$  in contrast to the substantial leachings of solvated silica that were accompanied by fluorine in equivalence to as much as 1,240 pounds of calcium fluoride, the release and migration of silica from the slagged soils was considered as a possible explanation for the high recovery of fluorine. That high recovery represented 47 per cent of the

TABLE 5

*Solvated silica carried by five annual rain-water leachings from 20-ton  $\text{CaCO}_3$ -equivalent incorporations of 100-mesh limestone, quenched calcium silicate slag, and wollastonite into two soils\**

INCORPORATIONS	$\text{SiO}_2$ LEACHED PER 2,000,000 POUNDS OF SOIL											
	Hartsells fine sandy loam						Baxter silt loam					
	1940	1941	1942	1943	1945	5-yr. total	1940	1941	1942	1943	1945	5-yr. total
	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.
Limestone.....	0	24	13	10	10	57	4	17	13	7	0	41
Quenched slag.....	97	67	118	109	140	531	69	49	102	88	125	433
Wollastonite.....	39	112	121	93	125	490	25	116	134	93	118	486
Rainfall, inches....	35.8	55.0	50.0	51.3	53.7	...	35.8	55.0	50.0	51.3	53.7	...

\* Those of group L in tables 3 and 4.

1,280-pound maximal input of fluorine as a slag component, in contrast to the 2.6 per cent recovery from the 2,400-pound input supplied as precipitated  $\text{CaF}_2$ .

#### OUTGO OF SOLVATED SILICA

Since it appeared that the migration of solvated silica might serve to promote the leachability of fluorine in either simple or complex combinations, the silica contents of the leachings from the 20-ton  $\text{CaCO}_3$ -equivalent incorporations of 100-mesh slag, wollastonite, and limestone in the Hartsells and Baxter soils of the L group of tables 3 and 4 are shown in table 5. The glassy quenched calcium silicate slag and the crystalline calcium silicate wollastonite exhibit distinctive carbonatations when they are suspended in  $\text{CO}_2$ -charged aqueous systems (21) and then register disparate reactivities in soil systems (4, 7, 19, 20, 21).

Although the outgo of silica from the fluoride-free wollastonite was similar to that from the fluoride-bearing slag, this similarity is not an index of the persistence of the two silicate materials after they are introduced into the soil. During

the initial year of the 6-year experiment, the 20-ton incorporation of the glassy slag underwent 60 per cent carbonatation—with corollary release of fluorine, presumably as dispersed calcium fluoride or as fluosilicate—whereas the equivalent incorporations of wollastonite imparted virtually no increase to soil content of  $\text{CaCO}_3$ . Thus, although the two forms of calcium silicate register differently in the generation of  $\text{CaCO}_3$  in the soil, they show alike in calcium bicarbonate outgo and in the migration of liberated silica. Since the slagged soils and wollastonite-treated soils yielded comparable leachings of silica, the large outgo of fluorine from the slagged soils cannot be explained conclusively by the postulation of leachings of calcium silicofluoride, yet the findings do not invalidate that postulation. It remains to be demonstrated whether a prefatory incorporation of calcic, and magnesian, materials would destroy the capacity of a soil to effect the fixation of additive fluorine when the addition is made as  $\text{CaF}_2$  or through the incorporation of superphosphate.

The disparity between the meager outgo of fluorine from the cumulative 2,400-pound incorporation of calcium fluoride in the phosphated and moderately limed soils and the substantial outgo from the smaller inputs of fluorine in the slagged soils may be attributable to two factors, separately or as joint considerations. Since aluminum compounds demonstrate distinctive affinities for fluorides under certain conditions, one factor relates to differences in the effectiveness of added liming materials to nullify capacity of aluminosilico soil complexes to fix fluorine. Such differential effectiveness is governed by perfection of distribution of the incorporated materials, by rates, and by rapidity of their disintegrations, which is influenced by particle size and by structure, since the quenched glassy compounds undergo dissolution more readily than the air-cooled and the mineral crystalline analogues. Even with most careful mixing, particles of the moderate incorporations of limestone and dolomite unavoidably were spotted throughout the soil, and hence there were many Ca-unsaturated soil areas in which fixation of the fluorine of the successive  $\text{CaF}_2$  incorporations might have occurred. When a particle of slag suffered hydrolytic disintegration, however, the released fluoride or silicofluoride was in intimate contact with quickly engendered solid carbonate or was bathed by or dissolved in a calcium bicarbonate solution that carried solvated silica and thus was afforded protection against fixation by aluminosilico complexes in the soil. This postulation would find support should it develop that comparable retentions of fluorine are effected by soils when calcium fluoride additions are made after soil saturations are induced and maintained through heavy incorporations of carbonate and silicate forms of calcium and of magnesium.

An alternate explanation is that the disintegration of the quenched slag results in the release of a colloidal form of either calcium fluoride or calcium silicofluoride that is far more dissolvable than the crystalline form of the pulverulent calcium fluoride. Obviously, the disintegration of the incorporated slag imparts to the liberated fluoride a dispersal far greater than that afforded by a mechanical distribution of the crystalline  $\text{CaF}_2$ , and therefore the slag-derived fluoride is subject to far greater "surface effect."

The findings demonstrate that, under one major condition, moderately lime-

stoned and dolomited soils retained virtually all of the fluorine that was incorporated in form intended to simulate inputs that would have been supplied through heavy incorporations of phosphatic fertilizers and that, under another major related condition, soils gave ready and substantial leachings of component fluorine after its liberation from incorporations of slag. Nevertheless, the absorptive capacities of substrata are such that the leachings of fluorine from heavily phosphated soils, and from those slagged, will not impart to ground waters a fluoride concentration to be considered as constituting a health hazard.

#### SUMMARY

After 10 years of lysimeter leachings from 51-inch annual rainfall, nine variously phosphated soil systems showed 98 per cent retention of the fluorine from cumulative incorporations of 4,932 pounds of precipitated  $\text{CaF}_2$  per acre. The retentions were far beyond those attributable to the formation of fluorophosphate. The drainage waters gradually attained fluorine concentrations of 1 to 2 p.p.m., when the fluorine inputs had aggregated 1,120 pounds. The 2-ton incorporations of rock phosphate yielded only 3.5 pounds of fluorine, with leaching concentrations invariably below 0.15 p.p.m. The moderate supplements of limestone and of dolomite induced slight increases in fluorine outgo from the rock phosphate and tricalcium phosphate incorporations, but not from the dicalcium phosphate and the metaphosphate.

In contrast, the calcium silicate slag incorporations on unphosphated soils yielded ready and substantial outgo of fluorine, which was accompanied by solvated silica and Ca bicarbonate resultant from the speedy hydrolytic disintegration of the slag and the carbonatation of the fraction of its calcium not sorbed by the soil. The 6-year outgo of fluorine from the 1,280-pound maximal input of fluorine on the slagged soils amounted to 14 times the 10-year outgo from the 2,400-pound inputs supplied through the cumulative addition of 4,932 pounds of  $\text{CaF}_2$ . The leachings from the slagged soils attained fluorine concentrations four times those shown by saturated aqueous solutions of calcium fluoride. Since x-ray examinations of the slag did not register incidence of calcium fluoride, a silico complex component may have been causal for the greater outgo of fluorine from the slagged soils. But the quantities of solvated silica that passed from the fluoride-free controls of wollastonite were comparable to those that passed from the equivalent incorporations of slag, and hence it is not proved that the enhancement in fluorine outgo from the slagged soils was induced by a concomitant outgo of the silica that was liberated upon disintegration of the incorporated slag. The almost complete retention of fluorine by the lightly limestoned and phosphated soils was from an inmixed crystalline fluoride, whereas the fluorine outgo from the slagged soil was from a content disbursed through the disintegration of the glassy material, the heavier incorporations of which apparently diminished greatly the capacity of the alumino soil complexes to effect fluorine retention.

Since the high concentrations of fluorine in the leachings from 10- and 20-ton upper-zone incorporations of slag were diminished 80 per cent during 6 years' gravitational passage through a corresponding zone of untreated soil, it is believed



that no harmful concentration of fluorine would develop in the ground waters from incorporations of slag or of phosphatic fertilizers.

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## MEASUREMENT OF THE WATER-STABILITY OF SOILS<sup>1</sup>

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Progressive deterioration of soil structure usually accompanies continuous cropping to clean-tilled crops. It is noticeable most frequently in soils of heavy texture and may be associated with the appearance of subsoil in the zone of tillage as a result of erosion. Other unmistakable evidences of physical deterioration of the surface soil are more ready slumping of the soil upon wetting, and hardness and intractability upon drying. Productivity is reduced. The deterioration in either case is associated with a lowered water-stability of the soil aggregates. It is probable also that retention of the favorable structure produced in soil by tillage depends on the water-stability of lumps of considerable size that tend to resist disintegration when subjected to an excess of water. These may then act as mechanical reenforcement against slumping and puddling. On this basis we believe that attention should be directed toward water-stability, not only as a characteristic of discrete soil aggregates, but as a measurable property of soils.

Measurements of the water-stability of soil granules may be made by the drop test. Vilensky (6) used this method, and McCalla developed a procedure that has been useful generally in determining the relative water-stability of loessial soils (3, 4). The method, however, is not well adapted for use on many soils except on a qualitative basis. The presence of gravel in a soil may interfere seriously with operation of the test. Methods of aggregate analysis, essentially as described by Yoder (7) have been used more extensively.

The aggregate analysis procedures are designed primarily to give information on the amounts and size distributions of the water-stable soil aggregates. Summations of the percentages of water-stable aggregates larger than some arbitrary size may be used, however, to measure relative water-stabilities. Attempts to use aggregate analyses in this manner led to the conclusion that a simpler, more rapid, and more duplicable procedure could be devised for characterizing this soil property.

The procedure was developed to meet a problem at hand. Some of the results obtained have been published (1, 2).

### METHOD

The wet-sieving apparatus used in the investigation included a nest of two sieves each 5 inches in diameter and  $1\frac{1}{2}$  inches in height. The sieve screens were 10- and 35-mesh, U. S. Bureau of Standards series, corresponding to openings of 2 and 0.5 mm. Mechanical equipment raised and lowered the sieves 35 times a

<sup>1</sup> Cooperative investigations of the Office of Research, Soil Conservation Service, and the Maryland Agricultural Experiment Station, College Park, Maryland. Published as Scientific Article No. A178, Contribution 2079, of the Maryland Agricultural Experiment Station.

minute through a stroke length of  $\frac{3}{4}$  inch. The immersion jars had a 6-inch inside diameter.

Soil was prepared by crushing the air-dry sample to produce a high percentage of lumps about 4 mm. in diameter. The sample was put through round-hole sieves to separate the 5-3 mm. fraction. This became the subsample on which the water-stability analysis was made.

About 25 gm. of soil was taken for analysis. The lumps were distributed on the top sieve of the nest, lowered into the immersion jar, and allowed to soak 1 minute or longer until thoroughly wet. They were then wet-sieved for 2 minutes. The soil was kept completely submerged during soaking and wet-sieving. When the wet-sieving was finished, soil retained on the sieves was combined by washing it into aluminum cans of about 300 mm. capacity. Gravel caught by the top sieve was separated out in the washing process. A funnel about 8 inches in diameter and an atomizer type jet employing both air and water were used in

TABLE 1  
*Replicability of water-stability analyses*

SOIL	RANGE IN WATER-STABILITY OF SAMPLE GROUP	TOTAL NUMBER OF ANALYSES	STANDARD DEVIATION BETWEEN DUPLICATES
	<i>per cent</i>		<i>per cent</i>
Manor loam.....	46-96	34	1.07
Susquehanna silt loam.....	39-54	10	1.50
Beltsville loam.....	9-66	24	1.35
All three soils.....	9-96	68	1.24

the transfer of the retained soil. The soil was dried at 105°C. and weighed. Water-stability was calculated as the percentage of the sample retained by the sieves. A correction for gravel was made whenever necessary.

#### RESULTS

The replicability of analyses by this procedure is shown in table 1. The data are based on analyses in which all samples were run in duplicate. The types of soils studied are listed in column 1, and the range in water-stability exhibited by the samples in each group is shown in column 2. Method replicability is indicated by the standard deviations of column 4. Most important is the standard deviation between duplicates for the total data. It equals 1.24 per cent.

Additional data on a number of soils are given in table 2 to show percentage differences between duplicate analyses over a wide range of water-stabilities. The greatest differences amount to about 3 per cent. The standard deviation between duplicates for these samples is 1.14 per cent and for the combined data of tables 1 and 2, 1.20 per cent. These figures may be compared to the differences in water-stability within soil types, as shown in tables 1 and 2. Seemingly, statistically significant differences relative to soil physical condition are to be ob-



tained in many comparisons without undue replication of the analytical procedure.

The replicability of aggregate analyses obtained by the method of Yoder (7), modified in some details,<sup>2</sup> is indicated in table 3. The standard deviation between

TABLE 2  
*Water-stability of various soils under different conditions*

SOIL	DEPTH <i>inches</i>	COVER OR TREATMENT	WATER-STABILITY, DUPLICATE SAMPLES	
			<i>per cent</i>	<i>per cent</i>
Leonardtown silt loam....	...	Woods	92.23	92.04
	...	Eroded field	4.34	4.70
Sunnyside fine sandy loam.....	...	Clover sod	73.25	73.20
	...	Noneroded field	20.09	19.88
	...	Eroded field	4.12	5.25
Manor loam.....	1-2	Woods	95.77	95.60
	4-6	Woods	91.94	91.60
	6-8	Woods	57.83	59.93
	0-6	Garden, 2 years from woods	66.69	69.46
	0-6	Eroded field, abandoned	88.62	88.26
	0-6	Eroded field, cultivated	49.00	50.70
Chalfont silt loam.....	0-2	Woods	96.97	96.73
	2-4	Woods	95.56	96.33
	4-6	Woods	90.56	89.94
	6-8	Woods	81.11	84.13
	0-3	Garden, 20 years from woods	16.06	17.24
	3-6	Garden, 20 years from woods	37.75	35.50
	0-6	Garden, 1 year from woods	57.41	59.14
Evesboro sandy loam....	...	Woods	71.29	68.44
	...	Lespedeza	41.98	42.87
Beltsville loam.....	...	Soybean residues	43.82	41.86
	...	Soybeans, residues removed	11.42	10.89
Hyattsville loam.....	...	Strawberries, mulched	31.36	33.67
	...	Strawberries, bare	16.94	14.20

duplicates for all the data is 2.33 per cent. Comparison of this value with the standard deviation of 1.20 per cent for the data of tables 1 and 2 shows better replicability by the water-stability analysis.

<sup>2</sup> The analysis was made on a nest of four sieves of 10-, 18-, 35-, and 70-mesh, U. S. Bureau of Standards series. The sieves were 5 inches in diameter and 1½ inches high. The immersion jar had an inside diameter of 6 inches. Mechanical equipment oscillated the sieves through a stroke length of ¾ inch at a rate of 35 per minute. [See "Tentative methods for the determination of soil conditions," a mimeographed publication of the Division of Research, Soil Conservation Service, 1943.]

Since the standard deviations used to indicate differences in replicability of the two methods of analysis are based on duplicate analyses of single soil samples, the variance within method that would be imposed by differences in sample preparation is excluded from the comparison. The inclusion of the preparation variance (single analyses of samples prepared in duplicate) probably would increase the difference in replicability between the two methods. It is common knowledge that results of aggregate analyses are somewhat dependent on the proportions of coarse and fine material in the sample analyzed. The personal factor as it affects sample preparation is largely excluded in the water-stability procedure by selecting lumps of uniform size for analysis.<sup>3</sup>

TABLE 3  
*Replicability of aggregate analyses*

SOIL	RANGE IN AGGREGATION OF SAMPLE GROUPS	TOTAL NUMBER OF ANALYSES	STANDARD DEVIATION BETWEEN DUPLICATES
	<i>per cent</i>		<i>per cent</i>
Manor loam.....	58-98	336	2.48
Hyattsville loam.....	26-67	160	2.07
Croom gravelly loam.....	55-77	48	2.19
Beltsville silt loam.....	51-57	12	2.03
All four soils.....	26-98	556	2.33

#### DISCUSSION

The data presented show an improved replicability in water-stability analyses over typical aggregate analyses, but a further discussion of the purpose of the method is desirable in view of the closely related work of Russell and Feng (5). These authors show that water-stability may be characterized by two parameters—an initial stability to wetting, and a secondary stability or rate of disintegration that characterizes soil aggregates on continuation of the washing process. Our experience generally is in agreement with their data and conclusions. They suggest, however, that of the two variables the rates of disintegration should probably receive greater consideration than initial stabilities in evaluating the water-stability of soil aggregates.

From our point of view, measurements of initial stability are of more importance than measurements of rates of disintegration. This would not be true if our interest were centered on the resistance of discrete and water-stable aggregates. We feel that a corollary to the statement of Russell and Feng is that initial stabilities should receive the greater consideration where information is wanted on the water-stability of the entire structure of a tilled soil as that affects its

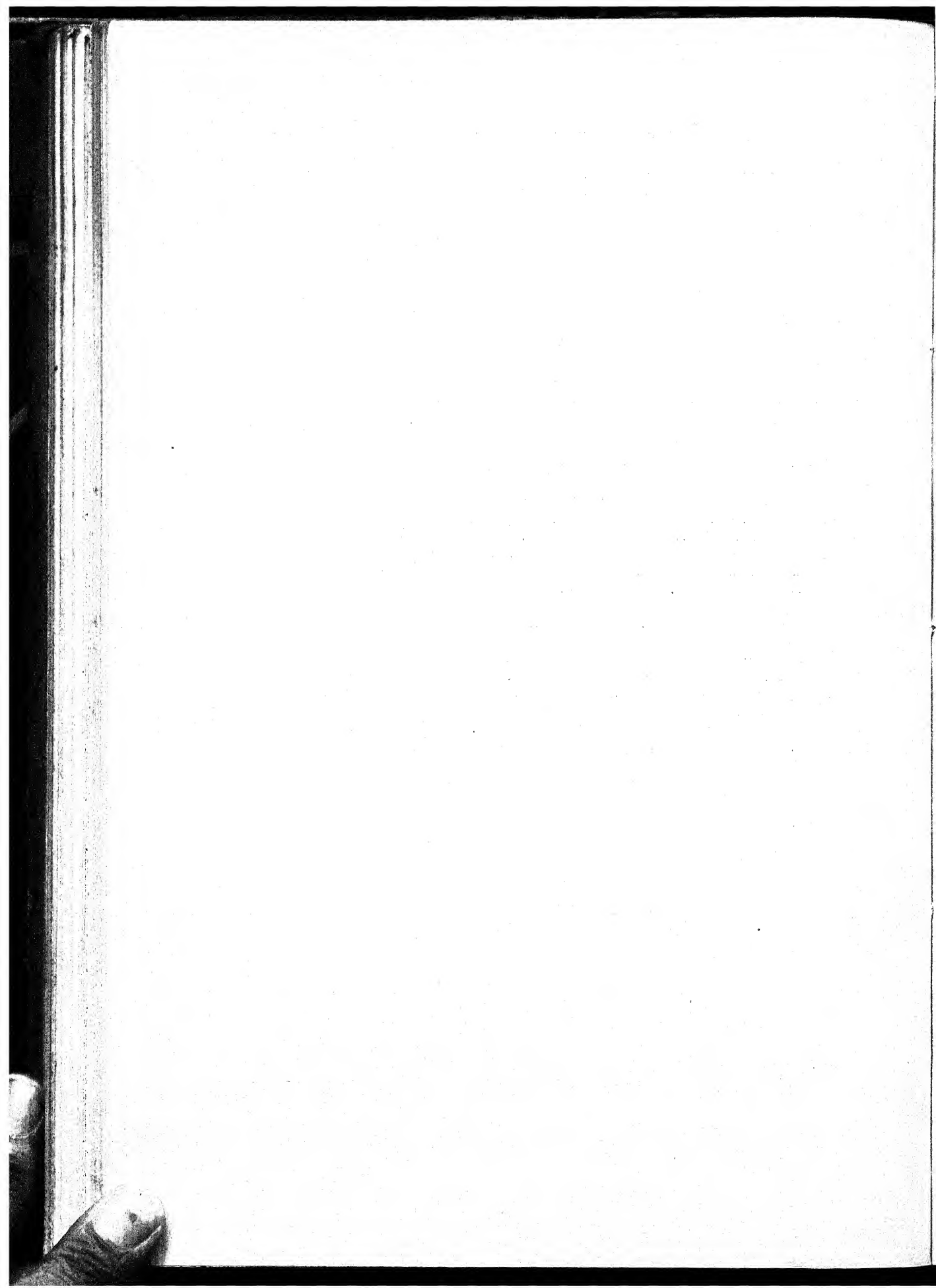
<sup>3</sup> In this connection, because of misconceptions we have encountered, it is necessary to note that the lumps selected for analysis are not discrete soil aggregates of a limited size range. Rather, they are small subsamples of the soil mass. Each lump may consist of any proportion of the water-stable and water-unstable components of the soil.

ability to resist slumping and puddling under field conditions of wetting and drying. It seems probable that the effects of different treatments to improve soil structure in this respect would be noted first in an improved bonding between aggregates in the water-unstable part of the soil, rather than in the bonding within discrete aggregates already stable to water. We consider that the initial stability of the lumps selected for analysis is a measure of such interaggregate bonding.

Admittedly, some splitting of hairs is involved in the preceding discussion. No sharp line of demarcation can be drawn between interaggregate and intra-aggregate stability. The data of Russell and Feng indicate that initial stabilities and rates of disintegration are correlated and are associated further with the size distributions of the water-stable aggregates. To some degree, therefore, all three appear to be measures of a common soil property. The finer distinctions are justified, however, in attempts to clarify the exact significance of the results of different procedures for examining structural properties of soils.

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## A NEW SOIL MOISTURIZING TECHNIQUE<sup>1</sup>

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Many determinations in soil physics, chemistry, and microbiology are subject to unknown factors resulting from variation in moisture distribution. The practice of atomizing water and applying it as a fog to dry soil is fairly satisfactory but is limited to a moisture range below the sticky point, since mechanical mixing, which may destroy the initial state of aggregation of the soil, is still necessary. Adding water to the soil in alternate increments is unsatisfactory because of the moisture gradient which cannot be avoided unless considerable time is allowed for the water to become uniformly distributed.

The difficulty of making up a soil to a desired moisture content has been recognized by Buehrer and Rose<sup>2</sup> and by Caster, Martin, and Buehrer.<sup>3</sup>

The method presented here involves the addition of water as ice scorings or snow to the dry soil at  $-20^{\circ}\text{C}$ . The desired amount of soil of known initial moisture content and uniformly mixed is passed through a 2-mm. screen. The soil is then taken to a deep-freeze room and spread out on a paper so that it will cool rapidly. While the soil is cooling, an amount of snow or ice from ice-scoring operations equivalent to the desired moisture content is passed through a 1-mm. screen. The snow-soil mixture is then carefully rolled until it is as uniform as possible. The sample is transferred to a tight container and returned to the laboratory. It is ready for use as soon as it warms to room temperature. (Transporting it after thawing may cause puddling.)

All moisturizing referred to was done in a commercial deep-freeze room. In cold weather the moisturizing could be done out doors.

Soils have been successfully prepared in a stable, unpuddled condition from air-dry to a moisture level higher than the moisture equivalent.

The following data show the moisture content of six 15-gm. samples taken at random from a 10-kgm. lot in which the weight of snow added was chosen to bring the samples to a moisture content of 19 per cent:

<i>Sample No.</i>	<i>% Moisture</i>
1	19.17
2	19.27
3	19.30
4	19.08
5	19.03
6	19.15
Average.....	19.17
Maximum spread.....	0.27

<sup>1</sup> This paper sets forth some of the results of an investigation being conducted under a fellowship grant from the Shell Chemical Corporation of San Francisco, California, and is published with the permission of that company.



These results indicate an unusual degree of uniformity of moisture distribution in view of the evident differences in particle size that exist in a soil sample screened through a 2-mm. sieve. They are particularly significant in view of the fact that the samples taken for the final moisture determination were of the order of 10 to 15 gm.

This method should find useful application in such soil studies as the following:

1. Preparation of soil samples, with uniform porosity, moisture, and structure, for microbiological incubations.
2. Calibration of tensiometers and soil conductivity bridges.
3. Soil color comparisons.
4. Making of uniform porous blocks for apparatus in soil physics.
5. Study of physical properties such as packing effects of soils at different moisture levels.
6. Study of soluble nutrient elements at low moisture levels.

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<sup>2</sup> Buehrer, T. F., and Rose, M. S. Studies in soil structure: V. Bound water in normal and puddled soils. *Ariz. Agr. Exp. Sta. Tech. Bul.* 100:185. 1943.

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## SOIL BACTERIA OF THE GENUS ARTHROBACTER<sup>1</sup>

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About 20 years ago one of the writers (1) described an organism as *Bacterium globiforme*, which has since come to be recognized (7) as a species, or more probably a larger group, of bacteria very abundant in soil. It is primarily characterized by the morphological peculiarity of appearing as a Gram-negative rod in young agar culture, and as a Gram-positive coccus in older cultures. Because of this striking type of morphology and of their abundance in soil, such bacteria have attracted considerable attention among soil bacteriologists, even though their significance is not yet determined.

*Bacterium globiforme* was regarded by Jensen (4) as quite likely a species of *Corynebacterium* (typefied by the diphtheria organism), and by Krassilnikov (5) as belonging to the genus *Mycobacterium* (typefied by the tubercle bacillus). Lochhead (6) was inclined to agree with Jensen, but not sufficiently so to place the species (or group) definitely in the genus in question. The present writers (2) have finally decided that the organism does not belong in either genus and have proposed reviving an old name, *Arthrobacter*, suggested by Fischer (3) as a *nomen nudum* (i.e., a genus without any species), and assigning to it the type species *Arthrobacter globiforme*. Two other species of this genus have been recognized by the writers, namely, *A. tumescens* and *A. helvolum*, both of which had been placed in *Corynebacterium* by Jensen.

Soil bacteriologists have been somewhat uncertain whether to regard "*Bacterium globiforme*" as a single species or as a group of several. This is largely because it has been distinguished mostly by negative characteristics, and the few positive physiological reactions obtained (e.g., acid from sugars in unbuffered media) have proved so variable as to be of little value for diagnostic purposes. Accordingly, in the writers' recent paper it still seemed unwise to recognize more than one species (namely, *Arthrobacter globiforme*) showing the type of morphology in question.

The object of the present brief note is to explain that one reaction has now been found which distinguishes some cultures from others and which has proved constant over a sufficient period so that it seems safe to use it as a basis of a specific distinction. That reaction is diastatic action on starch, as determined on starch-agar plates, tested with iodine after 7 days' incubation at 30°C. As the original description of *A. globiforme* specified diastatic action on starch, that name is retained for the species giving a positive reaction to this test. The name

<sup>1</sup> Journal paper No. 726. New York State Agricultural Experiment Station, Geneva, N. Y., October 31, 1947.

*Arthrobacter simplum* is hereby proposed for the species giving a negative reaction. The description of this species follows:

*Arthrobacter simplum*, n. sp.

*Short rods*: 0.4 to 0.6 by 0.6 to 0.8  $\mu$ , becoming coccoid in older cultures. In certain liquid media, branching forms with Gram-positive spherical granules are common. Non-motile. Rods usually Gram-negative; coccoid forms usually Gram-positive;

*Colonies on agar or gelatin*: Circular, punctiform.

*Agar slant*: Filiform, flat, smooth, soft, translucent, glistening growth, with translucent sheen.

*Broth*: Slight growth.

Nitrites produced from nitrates in synthetic agar media.

Glucose, sucrose, mannitol, and less readily lactose and certain organic acids utilized as sources of carbon and energy when grown in synthetic media. Acid production is often indicated in such media, but not in peptone media, and is probably due largely to carbon dioxide. No visible gas production.

No diastatic action on starch, as shown on starch-agar plates after 7 days' incubation.

Optimum temperature about 22°C.

The foregoing description differs from that of *A. globiforme* only in the absence of diastatic action on starch.

In addition to two nonchromogenic species, there are undoubtedly certain yellow chromogens which belong in the same genus and which occur in soil. One is the aforementioned *A. helvolum*. Secondly, there is a form (of which only a single representative has been found by the authors) that is just like *A. globiforme* except that it is lemon-yellow on agar. Thirdly, a few cultures have been found of an organism which is faint yellow in color and differs slightly in morphology from either *A. globiforme* or *A. helvolum*. Not enough representatives of either of the last two forms have been found as yet to justify describing them as distinct species. Finally, it has been learned from Lochhead that he and his associates have recorded the frequent occurrence of yellow forms among the cultures of the "Bact. globiforme group" which they have isolated from soil. They have not given specific names or descriptions to any of them.

Although these yellow forms seem to be scarce in the soils studied by the authors, such is not the case in regard to *A. simplum*. The latter seems to be only less abundant than *A. globiforme*—which is recognized as one of the most common soil species. Although the significance of this group is not yet known, the members are of interest not only because of their abundance in soil but also because of their peculiar morphology. This type of morphology seems to indicate relationships to the Actinomycetes and to the Corynebacteriaceae, though the authors are not willing to regard them as species of *Corynebacterium*. Undoubtedly they deserve more study. The sooner it proves possible to recognize definitely the various species which make up the group, the sooner we will be able to learn what their actual significance in soil may be.

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## BOOKS

*Chemical Insecticides.* Compiled by DONALD E. H. FREAR. Chronica Botanica Company, Waltham, Massachusetts: Stechert-Hafner, Inc., New York, 1947. Pp. 203. Price \$6.50.

This volume is a by-product of work begun during World War II at the Pennsylvania Agricultural Experiment Station as a preliminary to the search for new insecticides to replace those that had become scarce by reason of war restrictions. The purpose was to classify all the known chemical insecticides. In this book, which is volume 1 of a catalog of insecticides and fungicides, some 10,000 compounds and the biological tests that were employed are listed. Each chemical is given a code number, which is made up of numbers that have been assigned to the several constituent groups in the compound. The introductory chapter deals with the methods of arranging the compounds, their code numbers, and abbreviations employed. Other chapters include chemical insecticides, condensation-product insecticides, and miscellaneous insecticides. A list of references, an author index, and a numerical patent list are appended. The book is bound in heavy paper. It is a highly important contribution to the literature in this field.

*Elementary Nuclear Theory.* By H. A. BETHE. John Wiley & Sons, Inc., New York, 1947. Pp. 147, figs. 17. Price \$2.50.

This is a short course of 20 lectures on selected topics dealing with the problem of nuclear forces, as it was given at the research laboratory of the General Electric Company at Schenectady, New York. Its main headings are: descriptive theory of nuclei, quantitative theory of nuclear forces, and topics not related to nuclear forces, involving Beta disintegration and compound nucleus. The appendix contains an extended table on nuclear species. The book is not designed as a textbook but will be found very useful to those desiring an elementary knowledge of the topics covered.

*Human Breeding and Survival.* Revised Edition. By GUY IRVING BURCH AND ELMER PENDELL. Penguin Books, Inc., New York, 1947. Pp. 138. Price \$0.25.

The subtitle on this very disturbing little book is "Population Roads to Peace and War." The preface was written by Walter B. Pitkin, whose first sentence is: "Uncontrolled human reproduction not only favors the survival and the multiplication of the least gifted members of society; it menaces and in the long run will destroy human liberties and any chance for world peace." That, he says, is the thesis of the authors. Accordingly, the book deals with populations, their growth, the problems involved when they increase up to the limit set by the food supply, the extent to which controls, both natural and artificial, are in operation, and the problems that lie ahead unless more aggressive action is taken toward birth control. The book should be read by every man who specializes in the field of agriculture.

*An Introduction to Chromatography.* By TREVOR I. WILLIAMS. Chemical Publishing Company, Inc., Brooklyn, New York, 1947. Pp. 100, plates 8. Price \$4.

As a working guide to the use of chromatography for analytical purposes, this book will be of great interest to analytical chemists. Methods are given for standardizing alumina by the use of organic dyes. Detailed procedures are outlined for the isolation of vitamin K and certain other substances. Some of the illustrations are in full color. The nine chapters deal with principles, methods, absorbents, solvents, eluents, chromatography of colorless and inorganic substances, partition chromatography, examples, and theoretical considerations. A selected bibliography of 46 references is appended.

*Petrografia de los Suelos de la Provincia de Sante Fe.* By ANTONIO POCOVI. Publicacion Technia No. 59, Instituto Experimental, de Investigación y Fomento Agrícola-Ganadero, Provincia de Santa Fe, Argentina, 1947. Pp. 107, figs. 7, plates 3.

Results of the first of a series of mineralogical studies being made of the soils of the province of Santa Fe are reported in this publication. The mineralogical makeup of the several horizons of 21 profiles has been determined, and this is considered in relation to the geology, topography, vegetation, and climate of the area. It is shown that the profiles vary materially, not only in relation to location but from horizon to horizon. According to this study, eolian sediments deposited near the source of origin are composed mainly of the heavy minerals. In mature soils the proportion of heavy minerals is highest in the upper horizons. The alteration of minerals is always greatest in the upper horizons. Soils designated *rich* contain 3 per cent of heavy minerals and 10 per cent of light minerals rich in plant nutrients. *Poor* soils contain 1 per cent of heavy minerals and a low percentage of rich minerals. Among the rich minerals, the author includes biotite, muscovite, orthoclase, microcline, plagioclase, and apatite; and among the poor minerals, quartz, zirconium, rutile, and granite.

*Plants and Environment.* By R. F. DAUBENMIRE. John Wiley & Sons, Inc., New York, 1947. Pp. 424, figs. 87. Price \$4.50.

Designed for textbook use, this book on plant ecology is an outgrowth of notes that were employed in teaching students in botany, forest management, range management, and agriculture. It deals with those phases of geology, soils, climatology, and biology that affect the distribution and well-being of living things. Consideration is also given to the fire factor, the environmental complex, and adaptation and evolution. The material is interestingly and attractively developed. Each chapter is introduced with a detailed outline. Appended to the book are 612 references to literature cited. The book should be especially interesting to soil scientists in that it brings to bear a point of view that merits more consideration than is often given to it.

*Soil Freezing and Frost Heaving with Special Application to Roads and Railroads.*

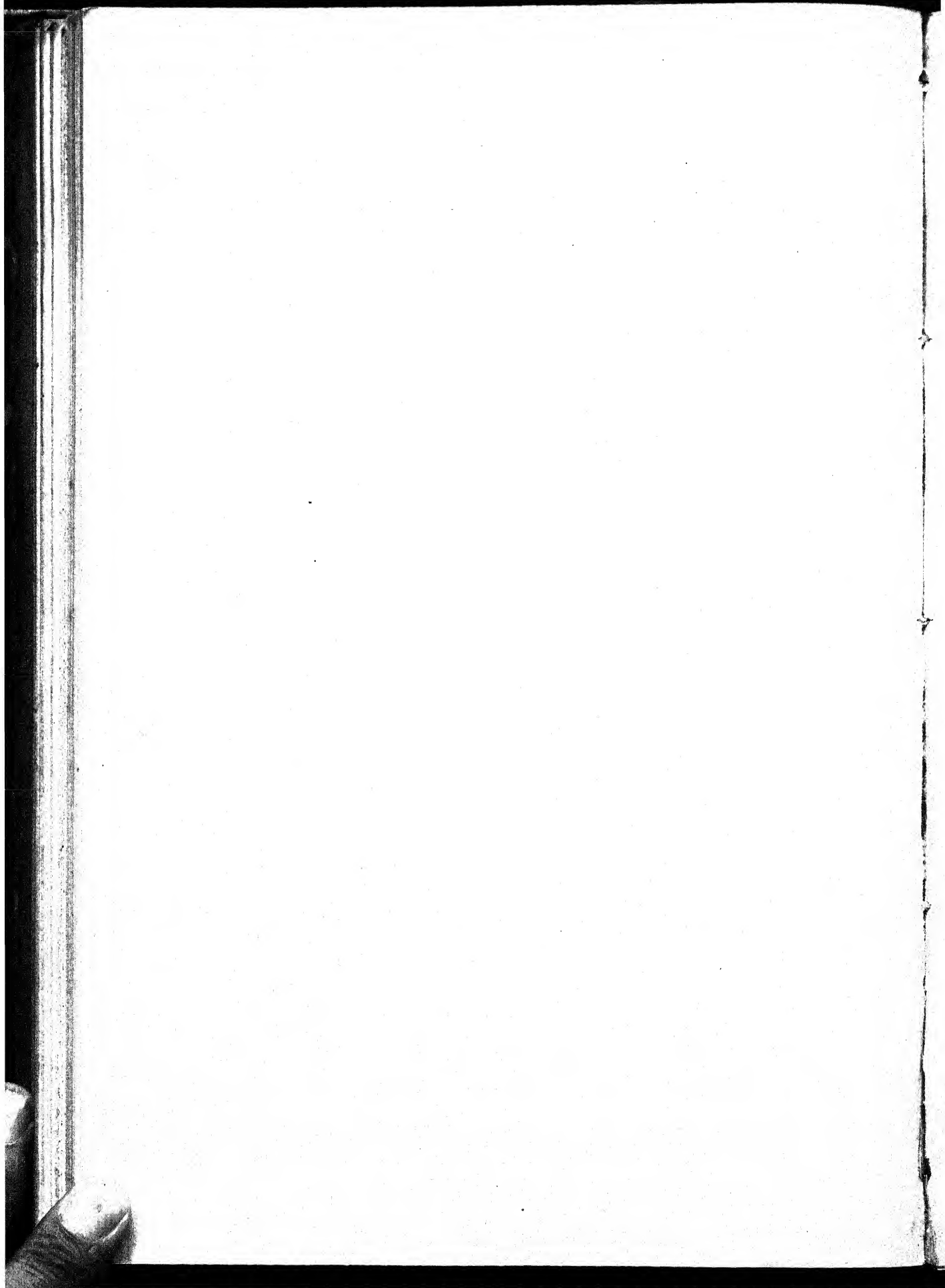
By FIL dr. GUNNAR BESKOW, Technological Institute, Northwestern University, Evanston, Illinois, 1947. Pp. 145, figs. 94. Price \$3.

This is a paper-bound, multigraphed translation of a treatise published in 1935 by the Swedish Geological Society, Series C, No. 375, 26th Yearbook No. 3, with a special supplement, for the English translation, of progress from 1935 to 1946. Its five parts are: historical introduction, mechanics of soil freezing, frost heaving, hydrodynamic considerations of frost heaving, and temperatures in freezing ground. A summary of the mechanical analyses of the soils used in the study is appended, and also a list of 85 references. The progress report deals with calculations of frost depth, freezing resistance of different materials, and practical measures against frost damage and adds 14 references. This highly important work is of interest not only to engineers dealing with highways and railroads but to those concerned with agricultural soils as well.

*Trees and Toadstools.* By M. C. RAYNER. Rodale Press, Emmaus, Pennsylvania, 1947. Pp. 91, plates 18. Price \$2.50.

This is a well-illustrated popular presentation on the subject of the mycorrhizal habits of trees. The book is divided into four parts dealing with the ways of life of trees and toadstools, the fungi of woodlands, the fungus-roots of trees, and the problems and partnerships involved. The history of the development of the mycorrhizal concept is especially interesting, and the illustrations employed in that connection are excellent. The book serves as a carrier of an advertisement for the Organic Gardening Magazine, which "contends that an infertile, unhealthy soil, caused by the use of chemical fertilizers, produces unhealthy plants and animals which when eaten produce unhealthy people."

THE EDITORS.



## THE SOILS OF EGYPT

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As Herodotus put it in 457 B.C., "Egypt is the gift of the Nile." The country as a whole forms part of a vast desert belt that extends from the Atlantic Ocean across North Africa and Arabia. The approximately 8 million acres of cultivable land in Egypt is a huge oasis in this barren, sandy desert. It is because of its fertile land, as well as its geographic position, linking the three continents of Asia, Africa, and Europe, that Egypt has been, from the dawn of history, a focus of cultural, economic, and political activities.

### AREA AND CLIMATE

The area of Egypt is 1 million square kilometers. This is approximately equal to that of Texas and New Mexico. The arable part of Egypt is about  $\frac{1}{3}$  of its whole area, the remainder being mostly barren desert, with a few scattered oases. The climate of Egypt is hot and dry in summer and warm and virtually rainless in winter. About 8 inches of rain falls in the winter on the Mediterranean shores. The annual precipitation decreases very rapidly southward. At Cairo, 100 miles from the Mediterranean Sea, it is only about 1 to 2 inches. Obviously then, agriculture, the pivot of the economy of the country, depends entirely on irrigation from the Nile.

### SOURCES OF THE NILE

The Nile rises from two main sources. Its main tributary, the White Nile, comes from the equatorial regions of Central Africa, especially from Victoria, Albert, and Edward Lakes. The average annual rainfall in these areas is 50 inches. The lakes act as natural reservoirs and provide the Nile with a constant supply of water during the year. The main flood of the Nile comes from the Blue Nile and Atbara Rivers, which have their origin in Abyssinia and join the White Nile in the Sudan. The level of water in these Abyssinian affluents is very low during the winter, but in summer, when more than 40 inches of rain falls between June and October, these tributaries become rushing torrents. This is the source of the annual flood of the Nile, which starts in Egypt in July, rises to a maximum in September, and then subsides to a minimum in the following April. The contributions of the aforementioned sources to the flood of the Nile are roughly 75 per cent from the Blue Nile, 15 per cent from the White Nile, and 10 per cent from the Atbara.

### THE ALLUVIAL MATTER

During the flood period, the water carries large amounts of suspended matter. Before the introduction of perennial irrigation in the nineteenth century, the

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Nile accrued annually about 8 tons of dry alluvial matter per acre. This deposit increased the depth of the soil at the rate of approximately 10 cm. per century

TABLE 1  
*Composition, quantity, and nature of suspended matter in the Nile, 1925-1927 (1)*

	JAN.	FEB.	MAR.	APR.	MAY	JUNE	JULY	AUG.	SEPT.	OCT.	NOV.	DEC.
<i>Chemical composition (percentage) of suspended matter at Cairo</i>												
SiO <sub>2</sub> .....	51.40	48.60	48.50	48.60	50.80	46.95	51.45	n.d.*	50.33	50.50	51.05	49.70
Fe <sub>2</sub> O <sub>3</sub> .....	9.04	11.28	11.08	10.35	10.40	8.91	9.51	n.d.	9.78	10.60	9.42	10.67
Al <sub>2</sub> O <sub>3</sub> .....	18.62	16.96	17.62	19.14	17.13	15.28	15.34	n.d.	18.72	18.68	19.76	18.54
TiO <sub>2</sub> .....	2.22	2.00	1.88	1.88	2.00	1.78	1.87	n.d.	2.11	2.30	2.27	2.20
MnO <sub>2</sub> .....	0.22	0.26	0.29	0.28	0.26	0.18	0.19	n.d.	0.23	0.22	0.24	0.25
CaO.....	4.18	4.75	4.25	3.66	3.25	5.31	4.12	n.d.	4.17	4.12	4.18	4.25
MgO.....	3.30	3.08	3.18	3.24	3.24	2.72	2.68	n.d.	3.52	3.34	3.38	3.43
K <sub>2</sub> O.....	1.02	1.02	0.92	0.98	0.85	0.82	0.80	n.d.	1.05	1.06	1.12	1.15
Na <sub>2</sub> O.....	0.92	0.63	0.60	0.55	0.82	0.82	0.78	n.d.	1.03	0.98	0.81	1.06
CO <sub>2</sub> .....	1.09	1.06	0.90	0.86	0.90	2.34	1.28	n.d.	1.01	1.00	1.09	0.90
P <sub>2</sub> O <sub>5</sub> .....	0.26	0.25	0.23	0.35	0.21	0.22	0.22	n.d.	0.24	0.23	0.24	0.26
Organic Matter†....	2.83	3.83	3.43	3.69	4.52	n.d.	n.d.	n.d.	2.62	2.45	2.34	2.38
N.....	0.22	0.14	0.28	0.35	n.d.	n.d.	n.d.	n.d.	0.13	0.12	0.15	0.13
<i>Total volume of water and total quantity suspended matter carried past Cairo</i>												
Volume of water†....	3.29	1.90	1.68	1.40	1.42	1.64	2.40	10.7	15.6	14.8	9.63	4.57
Total Suspended matter§.....	0.36	0.11	0.07	0.05	0.04	0.04	0.12	12.1	25.4	13.4	4.22	0.90
<i>Percentage distribution of suspended particles</i>												
	COARSE SAND		FINE SAND		SILT		CLAY					
Mean, flood months (Aug.-Nov.).....	0.2		18.5		26.3		55.0					
Mean, 8 months (Dec.-July).....	0.2		10.8		24.9		64.1					
<i>Exchangeable bases in suspended matter¶</i>												
Ca	Mg		K		Na		TOTAL					
37.7	13.2		1.0		0.3		52.2					

\* n.d. = not determined.

† C × 1.724.

‡ In cubic kilometers.

§ In millions of tons.

¶ In m.e. per 100 gm. dry matter.

(1, 2). The change in the system of irrigation, which is discussed later in this paper, caused a decrease in the amount deposited to between 0.5 and 1.5 tons (1).

Table 1 shows some properties of the suspended matter.

## BASIN SYSTEM OF IRRIGATION

The history of mankind is one of endless struggle with the elements. Undoubtedly, ancient Egyptians suffered severely from the fluctuations of the flood of the Nile. In seasons when the flood was below normal in height or duration, a considerable part of the land would remain uncultivated, whereas in seasons of high floods disastrous results would occur.

The first harnessing of the river was accomplished by raising the banks of the Nile and dividing the land into basins by use of earthen embankments. The water, about 1 meter in depth, was retained for 7 weeks, after which it was drained off into the Nile, as the level of the river subsided. On this water-soaked soil, sowing commenced in October and November. The land was given no more water until harvest time in early spring. This was known as the basin system of irrigation. It lasted without modifications until modern times, but now less than 20 per cent of the cultivated land of Egypt is under this system. The characteristics of the system, from the agronomic point of view, are as follows:

Only one crop is grown each year.

The fertility of the land is renewed by the alluvial matter (about 8 tons of dry matter per acre annually).

There is a rest period between harvesting of the crops in early spring and the next flood. During this fallow period the soil is subjected to drying, cracking, and aeration, with subsequent beneficial effects on microbial activity.

Drainage is maintained naturally.

## PERENNIAL IRRIGATION

The nineteenth century marked a revolutionary change, in that the basin system gave way to the perennial system, the advantage of which is that two or even three crops can be obtained each year. Instead of the bare land's being flooded only once a year to a depth of 1 meter for 7 weeks, the land is now watered at will all year round, according to the needs of the crops. The Nile pours huge amounts of water into the Mediterranean Sea during the flood period and it is very low in late spring and early summer. The problem of controlling the river is one of holding back the flood waters for use during the dry periods when water is badly needed.

Two great dams now provide a storage capacity of 7.7 billion cubic tons of water. Aswan, the first dam to be constructed, is one of the greatest achievements of modern times. It is situated about 600 miles south of Cairo and has a storage capacity of 5.5 billion tons of water. It is gradually filled between December and March. The sluices are reopened between May and July. The second dam, Gabal Aulia, on the White Nile to the south of Khartoum in the Sudan, was constructed in 1937 and provides a storage capacity of 2 billion tons of water. Masonry barrages were constructed across the river in Egypt to raise the water so as to allow an adequate flow in the canals that, through various ramifications, provide the land with water all year round.

It has been the policy of the Egyptian authorities: (a) to examine the whole

course of the Nile to obtain the utmost benefit from this mighty river, upon which the very existence of the country depends: (b) to minimize the enormous quantity of water lost each year into the Mediterranean Sea; (c) to convert all the remaining basin land (about 1 million acres) into perennially irrigated land; (d) to provide a system of efficient underdrainage.

#### SUITABILITY OF NILE WATER FOR IRRIGATION

Table 2 shows the composition of the dissolved solid matter in the Nile. Irrigation water containing a large amount of Na in proportion to its Ca and Mg has a deteriorating effect on soil. Kelley, Brown, and Liebig (5) concluded that the ratio<sup>2</sup> of Ca + Mg:Na should not be less than 1 if harmful effects of the Na are to be avoided. Magistad and Christiansen (6) pointed out that irrigation water with a salt content of less than 700 p.p.m. and a ratio of the sum of all

TABLE 2  
*Percentage composition of dissolved solid matter in the Nile (1)*

	JAN.	FEB.	MAR.	APR.	MAY	JUNE	JULY	AUG.	SEPT.	OCT.	NOV.	DEC.	YEAR (mean)
Ca.....	16.2	15.9	15.4	15.0	14.8	13.6	14.1	16.3	17.2	16.6	17.0	16.8	15.7
Mg.....	4.6	4.6	4.5	4.4	4.5	4.2	4.2	4.7	5.0	5.1	4.9	4.6	4.6
Na.....	10.9	11.3	11.3	12.0	13.5	16.3	17.0	11.8	7.8	7.2	7.6	9.1	11.3
K.....	2.1	2.2	2.1	2.2	2.5	3.2	4.2	3.6	2.5	2.3	2.2	2.1	2.6
Cl.....	7.3	8.2	10.6	12.0	10.7	9.6	9.0	5.6	3.0	3.2	4.8	5.5	7.5
CO <sub>3</sub> .....	31.3	30.8	28.9	27.0	31.5	36.8	38.0	29.8	29.8	26.6	31.3	30.8	31.2
SO <sub>4</sub> .....	5.2	5.4	6.3	6.6	6.2	4.9	5.0	5.8	5.5	4.7	4.6	5.1	5.4
PO <sub>4</sub> .....	0.2	0.2	0.2	0.2	0.1	0.1	0.2	0.3	0.3	0.4	0.3	0.2	0.2
SiO <sub>4</sub> .....	7.0	7.8	6.6	7.2	6.8	4.8	4.9	7.4	8.7	9.5	8.5	8.1	7.3
Total solids*...	162	175	196	216	217	212	200	140	138	132	138	154	
Ca+Mg:Na....	2.5	2.4	2.3	2.1	1.9	1.4	1.4	2.3	3.8	4.0	4.0	3.1	

\* In parts per million.

other cations to Na of not less than 1.7 is suitable for most plants under most conditions. If these figures are taken as criteria, it is evident that the Nile water is suitable for irrigation, for the total soluble salts range between approximately 130 and 220 p.p.m. and the ratio of Ca + Mg:Na is always greater than 1. Of course, in studying the suitability of water for irrigation, the anions present, the plants grown, the soil texture, the climate, and other factors must be taken into consideration.

#### EGYPTIAN SOILS

Egypt is conventionally divided into two parts. The Delta of the Nile constitutes what is known as Lower Egypt. The area to the south is Upper Egypt. The valley in the latter division forms a comparatively narrow strip along the

<sup>2</sup> All ratios referred to in this paper are cation-equivalent ratios.

stream with a width varying between 1 and 20 kilometers. In Upper Egypt there are about 2.3 million acres, of which about 1 million are still under the basin system. The Delta has an area of about 22,000 square kilometers, or nearly 5 million acres, of which about 3 million are at present cultivated. The remaining area includes shallow lakes and low-lying salty land.

From a pedological standpoint, the soils of Egypt are intrazonal, belonging to the division of fluviogenic or alluvial soils. They are young soils, no generalized pedogenic characteristics being attributable to them. The difference between the various types is a matter of texture and of the influence of management practices. It is common in such alluvial soils to encounter soil structure variation (2) caused by changes in conditions of deposition.

In studying soil fertility and soil deterioration, basin land is usually taken as the criterion, representing potentially the best (4). With a good structure, a high content of exchangeable bases (of which Ca is the dominant one), good drainage, and an annual contribution of alluvial matter, the fertility of the basin land has been maintained for centuries.

#### *Underground water level*

The improvement in irrigation was produced at the cost of an elevation of the underground water table. This became apparent as a result of the neglect of underdrainage. At the beginning of the nineteenth century the ground-water level in the middle of the Delta was 6 to 8 meters below the surface. In 1886 it had risen to between 3 and 4 meters below the surface. In 1908 it was only 1 meter below (3). The elevation was due primarily to infiltration from high-level canals. The first omen of the rising water table was a decrease in the average yield of cotton, the main crop of the country. Other crops also suffered declines in yield, but the effect was most pronounced with cotton because of the deep root system of that plant.

After 1912 the effect of the rise of the water table on the production of cotton was obscured by the invasion of the pink boll worm (2). During the last 25 years, the yield of cotton has again risen as a result of the introduction of new varieties and improvement in underdrainage, in farm practices, and in the methods of control of insects and fungus diseases.

#### *Evolution of saline soils*

According to the Russian system of classification, there are three important phases in the development of saline soils; namely, the solonchak, the solonetz, and the solodi.

The solonchak is characterized by:

Accumulation of salts, the exchangeable complex being usually saturated with the prevailing cation.  $\text{Na}_2\text{CO}_3$  may or may not be present.

No differentiation into horizons.

Very little structure.

Low humus content.

Leaching the solonchak, as a result of a fall in the level of the ground water, an increase in rainfall, or both, results in the formation of solonetz. In the majority of cases Na is the predominant ion, and the exchangeable complex is saturated with this ion.  $\text{Na}_2\text{CO}_3$  is formed as a result of the reaction of the Na-complex with  $\text{CaCO}_3$ , or by the hydrolysis of the Na-complex and the interaction of NaOH with  $\text{CO}_2$ . The soil becomes deflocculated, the fine particles moving to the B horizon where they are cemented to form a typical columnar structure. In some cases Mg or  $\text{Mg} + \text{Ca}$  may be the dominant cations, without change in the morphological features.

In general solonetz is characterized by:

Low salt content in the upper horizons.

Differentiation into horizons with a well-defined B horizon.

Saturation of the exchangeable complex with Na; Mg, also, may constitute a relatively large fraction of the exchangeable bases.

Solonetz is unstable. H ions enter the exchange complex upon hydrolysis. If this continues, it causes the gradual decomposition of the mineral complex with the release of silica, resulting in the third step of saline soil development, the solodi.

It is to be noted that the presence of  $\text{CaCO}_3$  or other Ca salts protects solonetz from degradation to the solodi, and brings the soil to a condition similar to that of normal soils. Also, any Ca-solonchak is transformed, when leached, into a normal soil, and not into a solonetz.

#### *Deterioration of Egyptian soils*

The infertile lands of Egypt may be divided, according to their origin, into two major groups, as follows: 1. Low-lying salty land bordering the Mediterranean Sea and the northern salty lakes. In this group, the shallow lakes and marshes in the lower Delta may be included. 2. Land that was fertile under the basin system and then deteriorated under perennial irrigation.

Since the introduction of large public-drainage projects in the last 25 years, both the government and individuals have reclaimed large areas of the first group. The amount of land that can thus be reclaimed depends to a large extent on the flow of the river in summer. The fate of the northern shallow lakes is eventual drying up and reclamation. In fact, one of the lakes has already been so reclaimed. Most of these lakes are now exploited for fishing. Plans have been suggested for diverting flood waters into certain of these lakes, thus building an annual deposit of alluvial matter that would otherwise be lost into the Mediterranean Sea (3). Gracie, and his colleagues (4) investigated soils of the second group and classified them into two main types: first, black alkali soils, formed in localities where the level of the subsoil water had risen nearly to the surface; second, gypsum-veined soils, formed in localities where the rise had not been so great as in the first type.

Tables 3 and 4 show some of the characteristics of the fertile and black alkali land. The dominant exchangeable base in the black alkali soils is Na, since the



TABLE 3  
*Exchangeable bases in fertile and black alkali land (4)*  
 Per 100 gm. air-dry soil

	Depth	Ca	Mg	Na+K	S.C.*	Ca+Mg	Na+K: S.C.	Ca:Mg
	<i>cm.</i>	<i>m.e.</i>	<i>m.e.</i>	<i>m.e.</i>	<i>m.e.</i>	<i>m.e.</i>		
Basin land	0-20	42.4	14.4	1.2	58.0	56.8	2.1	2.94
	20-40	42.3	15.0	0.6	57.9	57.3	1.0	2.82
	40-60	42.2	15.7	—	—	57.9	—	2.69
	60-80	42.3	15.8	—	—	58.1	—	2.68
	80-100	41.4	16.2	—	—	57.6	—	2.56
Fertile, perenni- ally irrigated land	0-20	27.8	12.4	1.2	41.4	40.2	2.9	2.24
	20-45	28.9	13.7	0.3	42.9	42.6	0.7	2.11
	45-70	27.4	16.5	—	—	43.9	—	1.66
	70-95	25.7	17.2	—	—	42.9	—	1.49
	95-105	25.9	18.2	—	—	44.1	—	1.42
Black alkali	0-15	5.7	4.3	27.2	37.2	10.0	73.1	1.33
	15-30	2.7	2.1	37.6	42.4	4.8	88.7	1.29
	30-55	2.0	2.5	37.1	41.6	4.5	89.2	0.80
	55-80	2.9	3.6	—	—	6.5	—	0.81
	80-105	5.1	6.7	—	—	11.8	—	0.76

\* Saturation capacity.

TABLE 4  
*Water-soluble constituents in basin and black alkali soils (4)*  
 Per 100 gm. air-dry soil

DEPTH	CO <sub>2</sub>	HCO <sub>3</sub>	Cl	SO <sub>4</sub>	Ca	Mg
<i>Basin soil</i>						
<i>cm.</i>	<i>m.e.</i>	<i>m.e.</i>	<i>m.e.</i>	<i>m.e.</i>	<i>m.e.</i>	<i>m.e.</i>
0.0-20	0.0	2.2	0.3	0.4	1.0	tr.
20-40	0.0	2.1	0.3	0.5	1.0	tr.
40-60	0.0	2.2	0.3	0.6	1.0	tr.
60-80	0.0	2.0	0.4	0.6	0.8	tr.
80-100	0.0	2.2	0.4	0.5	0.8	tr.
<i>Black alkali soil</i>						
0.0-15	1.4	6.7	0.0	1.8	0.0	0.0
15-30	3.7	4.8	0.0	1.1	0.0	0.0
30-55	2.5	6.0	0.0	0.8	0.0	0.0
55-80	0.0	10.4	0.0	0.5	0.0	0.0
80-105	0.0	8.3	0.0	0.5	0.0	0.0

Ca as well as the Mg has been precipitated as carbonate and silicate. In basin land the exchangeable Mg increases in relation to exchangeable Ca with in-

creasing depth; the increase being more pronounced in the fertile, perennially irrigated land and still more in the black alkali soils.

The term "black alkali" is used by many authors to denote soils that contain  $\text{Na}_2\text{CO}_3$ , because the carbonate dissolves humus with the resulting formation of black spots. According to Russell (7), the washing of Na-solonchak containing only small amounts of Ca seems to occur in three stages: (a) formation of black alkali land, typical of some irrigation regions; (b) development of the typical solonetz soils; (c) degradation of solonetz to solodi.

Russell considers black alkali an intermediate step between the true solonetz and Na-solonchak in irrigated areas. Those who have studied the black alkali soils of Egypt point out that these soils have no columnar structure. It is to be noted that such a structure can be observed only under dry conditions, which are rarely encountered in irrigated areas. According to the Russian classification, the black alkali soils may be found in solonchak, solonetz, and gradations between these two main divisions. In Egypt solonchaks, with the presence or absence of  $\text{NaCO}_3$ , have been reported.

#### *Biological role in the formation of black alkali soils*

Gracie et al. (4) have suggested that "the production of black alkali soils in Egypt in conditions of poor drainage takes place in a medium already rendered alkaline through the activities of sulfate-reducing bacteria." The formation of blue zones of ferrous compounds around the roots under poor drainage conditions attracted attention to these reducing bacteria. As a result of their action, sulfides are formed, which are alkaline in reaction. This increased alkalinity makes conditions more favorable for precipitation of replaced Ca and Mg as carbonates and silicates. There is no doubt as to the presence of such bacteria, but the extent and importance of their role is as yet not quite clear. Balls (1) reported that the Giza farm had up to five times as much NaCl in its subsoil water in 1933 as it had at the same places and same depths in 1913, 2 years after the canals on its margin had been converted into perennial flow. The underground water level is far from being stagnant. Its rise provides conditions for salt accumulation and solonchak formation. The fluctuations of level provide leaching and resalinization, with the resulting degradation of these solonchaks in the solonetz direction and then regeneration.

#### *Gypsum-veined soils*

Gypsum-veined soils constitute a peculiar type of evolution. The characteristic feature of this group is the presence, at a variable depth, of an impermeable layer that is generally, but not always, underlain by a horizon that is veined with gypsum and of good structure (4). The extent of the distribution of this type is not clearly known, but, in general, it is found in places that are not subject to very high water-table levels. The salt content is greater in these soils than in normal soils, and there is a peak of salt concentration in the veined horizon. In most cases the veined horizon is underlain by Na-clay. It is to be noted that fluctuations of the underground water-table, change in the composi-

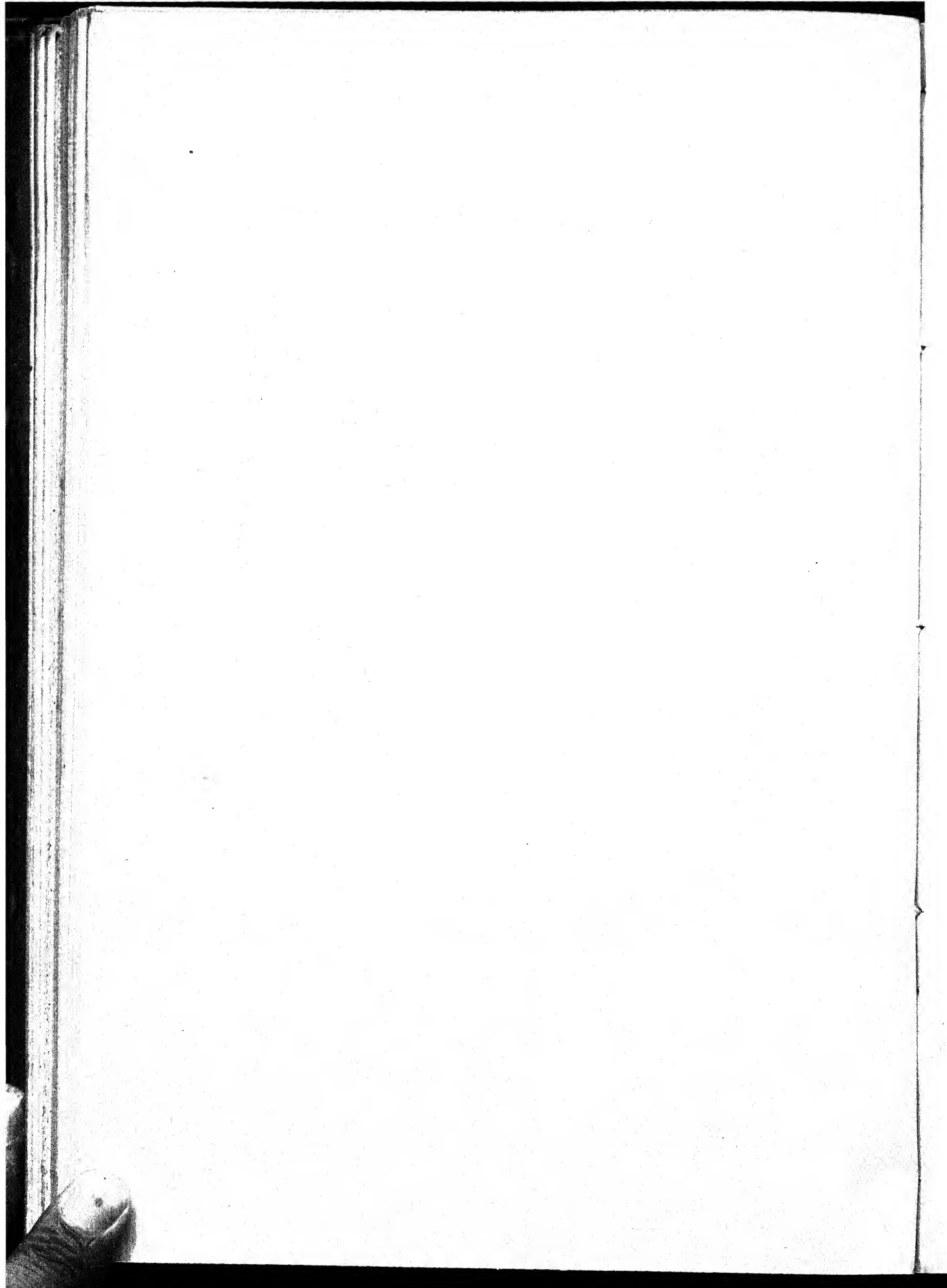
tion of this water, and structure variations often encountered in the soil (2) make the picture exceedingly complicated. The gypsum-veined soils appear to be similar to what the Russians call "hidden solonchak," yet further studies are needed to elucidate the conditions under which the impermeable layer is formed.

#### *Drainage*

It is a well-known phenomenon in all irrigated areas that whenever drainage does not go hand in hand with irrigation, salt accumulates in the soil with ensuing detrimental effects. In Egypt it is regrettable that drainage projects did not begin until after crops had suffered a great decline in yield, following the development of bad physical conditions in the soil. Since World War I, large drainage systems have been constructed by the government throughout the Delta along the low contours. It is the field drains, mostly 20 meters apart and 80 cm. deep, that have the beneficial effect on the soil. All the other drains are merely collectors that carry the salt water to the powerful drainage stations at the north of the Delta. These stations are in operation day and night, pouring huge amounts of drainage water into the Mediterranean Sea and northern lakes. More than 1 million acres in the Delta now benefit from these drainage projects. Eventually it should be possible to cover the whole country with a network of efficient drainage, thus restoring soil fertility and preventing further deterioration of the land.

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## LYSIMETER STUDIES WITH CULTIVATED AND VIRGIN SOILS UNDER SUBHUMID RAINFALL CONDITIONS<sup>1</sup>

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Lysimeters of the Ebermayer type used by the Russians, as described by Joffe (3), were installed on the experimental farm at Pullman in the fall of 1936 for the purpose of contrasting percolation losses from a cultivated soil under a pea-wheat rotation with those from a virgin soil with bunchgrass vegetation. Despite the strong criticism directed at the Russian type of lysimeter by Collison (1) and Kohnke, Dreibelbis, and Davidson (8), it is felt that this type of installation has yielded considerable valuable information that would not have been obtained with the filled-in or block type.

### DESCRIPTION OF INSTALLATION

Two pits, each 3 feet wide, 5 feet deep, and 11 feet long, were dug, and funnels, with the exception of the lateral funnel, were installed as described by Joffe (3). The funnels were made of heavy dairy tin instead of block tin and were filled with crushed quartzite fragments ( $\frac{1}{4}$  to  $\frac{3}{8}$  inch) instead of quartz pebbles.

The lateral funnel, designated "Lat." in the various tables of data, was essentially a cylinder 12 inches in diameter and 2 inches deep which was placed on its side so that its open end was in a vertical position and faced uphill. Its position in the profile was such that half of its area was in what is described later as horizon III and half in horizon IV. The outlet of this cylindrical funnel was at the lowest point of the cylindrical surface adjacent to the closed end of the cylinder.

The edges of the funnels were 24 inches from the wall of the pit. A wooden wall was built directly against the vertical soil cut. The funnels set in at the various depths were in triplicate except for those below the B horizon, which were in duplicate, and the lateral funnel, of which there was only one (fig. 1).

One of the pits was located in a cultivated area known as Crop Rotation Field 16D of the Experiment Station Farm; the other was approximately 35 feet east on the same hillside in a virgin area that had been preserved in its natural bunchgrass vegetation. The site has a southerly exposure and a slope of approximately 21 per cent. Just below the lysimeter installations are run-off plots of the Soil Conservation Experiment Stations together with rain gauges for obtaining precipitation records. In the spring of 1937 the slope above the cultivated lysimeter was seeded to *Agropyron inerme*, a plot area of only 15 feet in all direc-

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tions being left around the lysimeter pit, which was kept in the pea-wheat rotation. The total length of slope above the lysimeters ranged from 150 to 175 feet. The cropping practices followed are shown in table 1 together with the mean annual precipitation from August 1 to July 31, starting with 1936.

A description of the profile on the virgin area in which the lysimeters were installed follows:

Horizon I—0-4 inches—black when wet, dark gray when dry, thin platy structure, silt loam texture.

Horizon II—4-11 inches—color slightly lighter than I, granular to crumb structure, silt

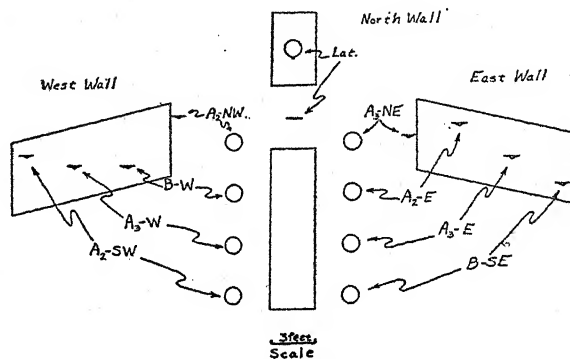


FIG. 1. DIAGRAM OF FUNNEL LOCATIONS

TABLE 1  
*Precipitation at the lysimeter site*

YEAR	CROP	PRECIPITATION	YEAR	CROP	PRECIPITATION
		<i>inches</i>			<i>inches</i>
1936-37	Wheat	19.79	1940-41	Peas	25.31
1937-38	Peas	16.76	1941-42	Wheat	18.98
1938-39	Wheat	16.57	1942-43	Peas	20.24
1939-40	Wheat	16.07			

loam texture. Funnels placed immediately below this horizon designated as A<sub>2</sub>-NW, etc.

Horizon III—11-29 inches—light brown, lumpy prismatic structure, silty clay loam texture. Lower portion contained streaks of white, siliceous material. Funnels placed immediately below this horizon designated as A<sub>3</sub>-W, etc.

Horizon IV—29-41 inches—light brown when dry, reddish brown when wet, dense, tough prismatic to massive structure, silty clay loam texture. Funnels placed immediately below this horizon designated as B-W and B-SE.

Horizon V—41 inches downward—compacted yellowish brown silt loam, containing scattered streaks of lime.

The profile in the pit of the cultivated area was identical except that horizons I and II were mixed by tillage to a depth of 8 to 10 inches.

## METHODS OF PROCEDURE

At the start of the experiment, all leachings from the various funnels were collected and brought into the laboratory after each rain. Later, when it became apparent that large volumes of leachate were available, the total volume was measured at the pit but only aliquots were taken into the laboratory. A portion was used for analysis of nitrate nitrogen and pH, and the remainder was set aside for further treatment.

During the early part of the experimental period an attempt was made to analyze every sample for each funnel individually for total solids, loss on ignition,  $\text{SiO}_2$ ,  $\text{R}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ , Ca, Mg, K, and P. It soon became apparent, however, from the large number of samples obtained that this was not feasible. Thereafter the analyses for these constituents were made on composites of the leachings for each drainage year, and in compositing, the replicate funnels were taken as a unit. Determinations of total nitrogen were also made on these composites. The analytical methods used were adapted from procedures described in the A.O.A.C. and elsewhere.

## EXPERIMENTAL RESULTS

*Hydrologic aspects*

In the light of lysimeter data reported under the heavier rainfall conditions in New Jersey and New York, the volumes of leachate obtained were surprisingly large. Tables 2 and 3 indicate this relation to be particularly true for the funnels below horizons III and IV. It is to be noted also that the deeper funnels drained more than the funnels beneath horizon II. Collison (1) noted a somewhat similar situation during certain rains and suggested that a "suction effect," as much as lateral movement of water and open channels of various kinds, was responsible for the greater percolation from the B horizons.

It is believed that in the Pullman experiment lateral flow is primarily responsible for the greater drainage from the lower funnels, since persistence of percolation for as much as 10 days after cessation of rain and the large volume of water drained could hardly be said to arise in the streamline volume (7) surrounding the funnel unless a lateral flow into the streamline zone continued to supply moisture of a lower tension than the suction tension provided by the funnel system. The magnitude of the drainage, particularly from the lateral funnels, emphasized the importance of lateral flow. The quantity of percolate from the lateral funnels was 3 to 25 times as great as from any other funnel, and percolation persisted for a longer time after the cessation of rain.

The data in table 4 indicate that one of the lateral funnels drained continuously for 73 days. The rate of flow of percolate from the lateral funnels was frequently of the order of 900 ml. per hour and at times even exceeded 1,000 ml. (equivalent to about  $1\frac{1}{2}$  inches per unit surface area of the funnel per hour). Such rates of flow approach what are considered erosive runoff values. Yet they cause virtually no soil loss within the virgin profile and only slight soil losses (approximately  $1\frac{1}{2}$  tons of total solids per acre of lateral funnel surface per

season as a maximum) within the cultivated profile. The pedogenetic significance of such rates of flow within the soil profile are discussed later.

The hydrologic significance of lysimetric data for such flows lies in the possible

TABLE 2  
*Drainage data for lysimeters in cultivated area*

	FUNNEL DESIGNATION								Lat.
	A <sub>2</sub> -NW	A <sub>2</sub> -SW	A <sub>2</sub> -E	A <sub>2</sub> -W	A <sub>2</sub> -NE	A <sub>2</sub> -E	B-W	B-SE	
Volume collected, Feb. 26, '37-June 26, '37. ml.....	906	145	1,455	580	939	21	0	0	3,450
Number of collections..	5	2	4	2	2	1	0	0	2
Volume collected, Oct. 9, '37-Apr. 15, '38. ml.	5,923	497	2,574	8,337	556	668	13,088	1,090	36,970
Number of collections..	5	3	5	7	3	2	11	2	11
Volume collected, Feb. 16, '39-Mar. 27, '39. ml.....	2,200	0	1,250	12,455	2,060	0	9,710	0	108,990
Number of collections..	2	0	2	6	2	0	4	0	9
Volume collected, Jan. 5, '40-Mar. 19, '40. ml.	3,097	1,275	1,120	12,300	0	132	47,600	4,782	72,746
Number of collections..	6	2	2	5	0	1	15	3	14
Volume collected, Oct. 5, '40-Mar. 19, '41. ml.	10,195	7,643	577	34,635	11,030	3,084	38,610	16,310	442,191
Number of collections..	10	6	4	24	7	2	61	7	79
Volume collected, Dec. 19, '41-Feb. 25, '42. ml.....	4,536	899	530	20,371	2,536	0	15,074	10,191	193,445
Number of collections..	6	4	1	13	3	0	19	9	20
Volume collected, Nov. 18, '42-Apr. 3, '43. ml.	20,823	12,590	1,430	46,297	40,930	470	3,576	44,425	405,365
Number of collections..	13	10	4	17	12	2	4	13	34
Total volume collected, Feb. 26, '37-Apr. 3, '43. ml.....	47,680	23,049	8,936	134,975	58,051	4,375	127,658	76,798	1,263,157
Total number of collections.....	47	27	22	74	29	8	114	34	169

contribution to an interpretation of the nature of a dynamic subsurface storm flow which was described by Lowdermilk (9) as being neither true overland storm-runoff nor true ground-water discharge. Hursh and Brater (2) have described a subsurface-flow in which there is relatively shallow penetration of storm water

into porous upper soil horizons and its rapid lateral flow with the slope to natural outlets, the true water table possibly taking no part in the phenomenon. Such apparently is the case with the lateral flows which were measured in the lysimeter.

TABLE 3  
*Drainage data for lysimeters in virgin area*

	FUNNEL DESIGNATION								Lat.
	A <sub>2</sub> -NW	A <sub>2</sub> -SW	A <sub>2</sub> -E	A <sub>2</sub> -W	A <sub>2</sub> -NE	A <sub>2</sub> -E	B-W	B-SE	
Volume collected, Apr. 16, '37-Apr. 21, '37. <i>ml.</i>	0	0	0	0	335	0	0	897	0
Number of collections..	0	0	0	0	1	0	0	2	0
Volume collected, Nov. 26, '37-Apr. 15, '38. <i>ml.</i>		10	313	13,586	14,570	7,490	3,256	503	37,709
Number of collections..	0	1	2	6	6	2	7	3	8
Volume collected, Nov. 18, '38-Mar. 27, '39. <i>ml.</i> .....	0	1,014	1,430	25,310	41,755	23,240	1,085	5,000	162,745
Number of collections..	0	2	2	10	11	8	2	2	14
Volume collected, Feb. 5, '40-Mar. 13, '40. <i>ml.</i>	3,684	0	73	15,794	22,300	12,530	0	5,141	107,080
Number of collections..	2	0	1	10	9	5	0	5	14
Volume collected, Nov. 29, '40-Mar. 19, '41. <i>ml.</i> .....	65	205	255	22,926	37,433	20,685	5,610	8,755	126,396
Number of collections..	1	1	1	19	16	10	21	28	63
Volume collected, Dec. 19, '41-Feb. 25, '42. <i>ml.</i>	55	0	485	15,313	34,139	24,611	3,848	15,967	115,655
Number of collections..	1	0	2	16	17	9	9	19	18
Volume collected, Nov. 18, '42-Apr. 3, '43. <i>ml.</i>	1,170	200	1,872	94,200	120,166	73,092	1,560	84,364	370,444
Number of collections..	3	1	2	28	27	20	3	27	33
Total volume collected, Apr. 16, '37-Apr. 3, '43. <i>ml.</i> .....	4,974	1,429	4,428	187,129	270,698	161,648	15,359	120,627	920,029
Total number of collec- tions.....	7	5	10	89	87	54	42	86	150

During the fall of 1941 some simple test wells were sunk to ascertain the sub-surface flow conditions downslope from the lysimeters. The test wells were made by boring a hole with a posthole auger through horizons I, II, and III to the top of the compact layer. A piece of corrugated downspout pipe 4 inches in diameter

was then driven into the hole so that the open bottom end was sealed by the compact horizon (fig. 2).

Approximately 3 inches above the lower end of the pipe eight slits ( $\frac{3}{8}$  inch by

TABLE 4  
*Duration of flow from lateral funnels*

DRAINAGE YEAR	PLOT LOCATION	DATE OF START OF FLOW	DATE OF END OF FLOW	DURATION OF FLOW
				<i>days</i>
1936-37	Cultivated	Apr. 16	Apr. 18	2
1937-38	Cultivated	Dec. 31	Jan. 2	2
	Cultivated	Jan. 22	Apr. 5	73
	Virgin	Jan. 22	Feb. 25	34
	Virgin	Mar. 14	Mar. 30	16
1938-39	Virgin	Feb. 15	Feb. 21	6
	Virgin	Mar. 2	Mar. 27	25
	Cultivated	Mar. 11	Mar. 27	16
1939-40	Cultivated	Feb. 7	Feb. 9	2
	Virgin	Feb. 17	Feb. 18	1
	Cultivated	Feb. 25	Mar. 13	17
	Virgin	Feb. 25	Mar. 13	17
1940-41	Cultivated	Nov. 27	Dec. 7	10
	Virgin	Nov. 30	Dec. 7	7
	Cultivated	Dec. 21	Jan. 8	18
	Virgin	Dec. 21	Jan. 8	18
	Cultivated	Jan. 18	Mar. 15	57
	Virgin	Jan. 18	Feb. 20	33
	Virgin	Mar. 3	Mar. 9	6
1941-42	Cultivated	Dec. 19	Dec. 24	5
	Virgin	Dec. 19	Dec. 24	5
	Cultivated	Jan. 28	Feb. 20	23
	Virgin	Jan. 28	Feb. 25	28
1942-43	Cultivated	Nov. 24	Nov. 28	4
	Virgin	Nov. 26	Nov. 28	2
	Cultivated	Dec. 1	Jan. 11	42
	Virgin	Dec. 1	Jan. 11	42
	Cultivated	Feb. 9	Mar. 4	23
	Virgin	Feb. 9	Mar. 5	24
	Cultivated	Apr. 1	Apr. 5	4
	Virgin	Apr. 1	Apr. 5	4

4 inches) had been cut into the valleys of the corrugations with an oxyacetylene torch. Laterally flowing water could enter the pipe through these slits and rise in the pipe. The height of water in the pipe was determined with a suitable measuring stick.



On December 18, 1941, drainage began from several funnels in the lysimeter pits. On December 19 rapid lateral flow began but slowed and stopped in two days. On January 28, 1942, rapid lateral flow again ensued and persisted until February 18. Well measurements were started on January 28. Lysimeter and well data are shown in table 5.

When the well was sunk on the virgin area it was noted that the siliceous and compact layers were less strongly developed than those at the well hole on the cultivated area. Apparently at the distances downslope from the lysimeter pits at which these wells were sunk, the vertical permeability on the virgin area was sufficient to distribute the moisture to greater depths in the profile. Here, in consequence, the lateral subsurface flow which occurred at the lysimeter sites, though to a significantly less degree on the virgin area than on the cultivated, as evidenced in the drainage from the lateral funnels, failed to persist.

As shown in table 5, a maximum free water head of 16 inches developed in the well on February 4. The average rate of flow of water through the lateral funnel for the preceding 48 hours was at least  $\frac{1}{3}$  inch per hour.<sup>3</sup>

Tolman (11) cites values of average field velocities of ground water in silt, fine sand, and loess as 0.065 feet per day at a hydraulic gradient of 1 per cent.

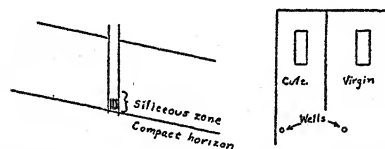


FIG. 2. LOCATION AND CONSTRUCTION OF TEST WELLS

Assuming a hydraulic gradient equivalent to the soil slope or 21 per cent, this would give a velocity of 1.365 feet a day. The rates obtaining at the time of the well observations were of the order of magnitude of 0.66 foot a day, but as the soil at the depth of the lateral funnel is silty clay loam, a value somewhat lower than 1.365 might be expected.

The virgin and cultivated areas show no consistent difference in volume of percolate from the respective horizons (compare tables 2 and 3). In general, the A<sub>2</sub> and B funnels in the cultivated area drained more than the corresponding funnels in the virgin area, whereas the reverse was true for the A<sub>3</sub> funnels. In four out of the seven drainage seasons the lateral funnel in the cultivated area drained more than the corresponding funnel in the virgin area.

A high degree of variability among the replicate funnels in the amounts of percolate obtained per rain and per season is readily apparent in tables 2 and 3. Such variability was similarly noted by Collison (1) and serves to indicate the irregular pattern of the percolation processes in a soil profile. Although the

<sup>3</sup> 14,000 ml. in 24 hours over a funnel area of 1/55,000 acre. Furthermore, in a cylindrical well the area of inflow would be equal to the area of outflow; hence, the hydrostatic head of 16 inches must represent the integration of forces necessary to cause rates of aqueous flow approximating that of 1/3 inch per unit area per hour.

variability prevents a highly accurate characterization of the eluviation processes, the strong differences between the nature of the percolates from the two areas (virgin and cultivated) warrant attachment of considerable significance to the data, as shown later.

### *Pedogenetic aspects*

The Palouse formation has intrigued the geologist for many years. Its unique conformation (dunelike) has elicited several theories of explanation. At the same time, this unique topography has posed puzzling questions to the soil scientist trying to explain the presence of various profiles found in traversing a single dunelike hill. It was felt that the Russian type of lysimeter might shed some light on the pedogenetic processes in the soil profile.

TABLE 5  
*Well measurements*

DATE (1942)	CULTIVATED AREA		VIRGIN AREA	
	Volume of leachate	Depth of water in well	Voumle of leachate	Depth of water in well
	<i>ml.</i>	<i>inches</i>	<i>ml.</i>	<i>inches</i>
Jan. 28.....	14,000+	8	14,000+	0
Jan. 29.....	10,550	7	7,900	0
Jan. 30.....	6,080	7	4,870	0
Jan. 31.....	3,350	6½	3,650	0
Feb. 3.....	14,000+	11½	14,000+	0
Feb. 4.....	14,000+	16	4,870	0
Feb. 5.....	14,000+	13½	10,350	0
Feb. 6.....	14,000+	11½	5,780	0
Feb. 10.....	7,900	6	3,950	0
Feb. 12.....	10,800	5	6,690	0
Feb. 14.....	7,600	2	4,870	0
Feb. 18.....	7,300	0	4,870	0

+ Crock overflowed prior to collection.

The physical forces of the pedogenetic processes have already been discussed to some extent under hydrologic aspects. Undoubtedly the magnitude and the intensity of water flow within the profile have contributed to the lateral transport of the colloidal clay fraction from steeply sloping areas to more gentle interslopes. Data reported by Kardos *et. al* (6) indicated that on steep northerly slopes considerably less clay was present in the 48-62-inch layer than in the compact layer immediately below it or the layer immediately above it. Such a textural anomaly within the profile could be accounted for by the lateral transport of the clay fraction to the interslopal basins. Accumulation of this clay fraction over a period of years has undoubtedly contributed to formation of the heavier, more poorly drained soil, such as the Caldwell, which is found in the interslopal basins. A more detailed study of this relationship would be of interest.

Some measure of the chemical forces operating within the soil profile is re-

flected in the pH values of the percolating soil fluids and the chemical composition of the colloid fraction which is moving from place to place within the soil profile. Table 6 presents data on some of the individual leachates obtained between February 26, 1937 and January 28, 1938; table 7, analyses of the composites for the leachate years of 1937-38, 1938-39, and 1939-40; and table 8,  $\text{SiO}_2/\text{R}_2\text{O}_3$  ratios of the composites and average pH values of individual horizontal leachate samples.

The data show a wide variation in  $\text{SiO}_2/\text{R}_2\text{O}_3$  ratio from a minimum of 1.03 to a maximum of 4.16, and no correlation between pH and  $\text{SiO}_2/\text{R}_2\text{O}_3$  ratio. The data indicate that the solvated and transported colloid tends to have a somewhat

TABLE 6  
*Composition of individual leachates*

LEACHATE NO.*	FUNNEL DESIGNATION	TOTAL SOLIDS	LOSS ON IGNITION	$\text{SiO}_2/\text{R}_2\text{O}_3$ RATIO	$\text{Al}_2\text{O}_3/\text{Fe}_2\text{O}_3$ RATIO	pH
		<i>mgm./100 ml.</i>	<i>mgm./100 ml.</i>			
1	A <sub>3</sub> -NE	23.30	—	3.03	14.02	6.8
2	A <sub>2</sub> -NE	40.35	—	2.27	1.76	7.8
3	A <sub>2</sub> -NW	26.30	—	3.30	2.10	7.2
3	A <sub>3</sub> -NE	23.40	4.43	1.15	4.87	7.5
3	A <sub>3</sub> -W	43.90	9.56	1.25	2.67	7.1
3	Lat.	94.30	8.69	3.18	0.48	7.3
3-V	B-SE	24.40	—	1.18	17.80	7.1
3-V	A <sub>3</sub> -NE	36.20	—	1.56	1.79	7.5
4	Lat.	45.62	—	1.91	20.30	7.3
11	A <sub>2</sub> -NW	30.20	12.56	4.72	0.35	6.8
11	A <sub>2</sub> -NE	48.52	9.78	4.07	0.02	6.7
11	A <sub>3</sub> -W	27.76	14.00	3.49	1.90	6.6
11	B-W	33.58	10.88	4.34	0.59	7.1
11	Lat.	24.29	9.78	3.08	2.09	6.7
11-V	A <sub>3</sub> -W	24.57	10.00	3.63	1.19	6.7
12	A <sub>2</sub> -NW	27.15	9.85	2.85	0.74	7.1
12	Lat.	19.71	8.58	3.40	2.03	6.8
12	B-NW	25.35	9.38	4.58	3.31	7.4

\* 3-V and 11-V frlm virgin area; all others from cultivated area.

narrower  $\text{SiO}_2/\text{R}_2\text{O}_3$  ratio than the whole clay fraction which was isolated from a similar soil by Kardos and Bowlsby (5). These workers reported values of 3.09 and 2.99 for the  $5\mu$  clay fractions from the A and B horizons respectively. It is probable that the material contained in the percolates consisted of both chemically solvated material and mechanically eroded ultraclay. Over the pH range 6.4 to 7.9, which represents the maximum range of pH of the individual percolates composited, the sesquioxides could be solvated both cationically and anionically. The data indicate, however, that aluminum is the chief sesquioxidic component and its anionic solvation could occur only as a partly silicated complex. The mechanically eroded clay would also be electronegatively charged and dispersed. Indirect evidence of the electronegative character of the suspended solids was the

nonadherence of the settled solids to the walls of the glass containers, which themselves acquire a negative charge with respect to aqueous media. The author in working at the New Jersey Station with percolates obtained from Joffe's

TABLE 7  
*Composition of lysimeter leachings*

FUNNEL DESIGNATION	COM-POSITE	TOTAL N	SOLIDS	LOSS ON IGNITION	SiO <sub>2</sub> AND HCl-IN-SOLUBLE MINERAL	SiO <sub>2</sub> LOSS BY HF	R <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	K <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>
1937-38*												
	per cent	mgm./l.	mgm./l.	mgm./l.	mgm./l.	mgm./l.	mgm./l.	mgm./l.	mgm./l.	mgm./l.	mgm./l.	mgm./l.
Cu-A	50	14.344	379.8	121.8	101.4	95.6	73.5	4.860	35.00	26.05	5.15	0.38
Cu-A <sub>3</sub>	50	13.253	225.8	106.2	24.4	23.6	28.5	2.220	28.74	19.35	3.12	0.33
Cu-B	25	10.120	252.0	113.6	30.6	28.8	19.0	1.812	28.00	23.15	0.94	0.26
Cu-Lat.	10	11.294	213.8	93.2	33.8	26.6	47.0	9.732	23.50	16.10	1.79	0.20
V-A <sub>3</sub>	10	2.207	165.2	28.0	66.6	61.2	27.0	5.700	7.30	12.50	1.00	1.30
V-B	80	2.098	193.8	67.6	38.4	26.2	14.5	1.308	12.00	12.65	2.53	0.58
V-Lat.	10	1.808	149.6	57.4	30.8	22.0	13.5	1.092	8.00	10.50	2.72	0.65
1938-39												
Cu-A <sub>2</sub>	68	9.793	613.4	121.2	240.4	222.8	139.0	36.996	33.32	24.25	1.10	0.64
Cu-A <sub>3</sub>	30	6.136	664.6	96.2	298.6	276.0	214.5	38.844	22.23	23.15	1.64	0.80
Cu-B	33	6.299	712.4	111.8	287.0	263.4	144.5	38.104	30.02	23.90	2.75	0.40
Cu-Lat.	4	5.353	650.4	105.6	264.2	245.2	228.0	45.180	22.14	26.45	2.33	0.98
V-A <sub>2</sub>	90	3.525	181.2	58.8	52.6	44.8	45.0	1.824	14.15	8.50	3.41	3.00
V-A <sub>3</sub>	5	3.166	178.0	55.4	50.6	43.4	52.0	1.416	12.09	9.25	2.93	1.10
V-B	80	3.101	214.4	34.4	69.6	60.6	43.5	2.172	16.62	10.30	2.54	1.40
V-Lat.	3	2.970	162.2	43.4	52.6	44.4	31.5	1.824	13.40	11.95	1.21	1.60
1939-40												
Cu-A <sub>2</sub>	45	12.666	561.2	134.0	193.2	173.6	150.0	33.932	34.56	78.5	15.52	1.20
CuA <sub>3</sub>	12	7.238	397.2	62.0	140.0	130.6	118.5	29.162	19.08	41.0	8.74	0.93
Cu-B	7	4.833	359.2	60.2	107.8	102.4	79.0	18.838	23.55	53.0	6.08	0.61
Cu-Lat.	3	7.984	345.6	66.8	120.2	115.4	95.5	25.322	17.66	45.0	7.53	0.98
V-A <sub>2</sub>	14	2.852	114.8	31.2	40.0	31.2	21.0	2.608	10.83	16.5	4.72	0.65
V-A <sub>3</sub>	7	3.044	132.0	29.0	57.2	46.6	23.5	4.164	12.31	31.5	2.19	0.56
V-B	35	2.298	163.4	43.0	56.6	39.6	30.5	4.736	18.55	28.5	3.33	0.59
V-Lat.	2.5	2.929	146.4	50.6	37.8	31.0	19.5	2.648	18.37	31.5	2.92	0.46

\* Insufficient V-A<sub>2</sub> for analysis in 1937-38.

lysimeters noted that the colloids tended to adhere very strongly to the walls of the flasks and could be removed only with difficulty with a rubber "police-man." The Palouse soil colloids, on the other hand, were easily rinsed from the containers.

The pedogenetic significance of the prolonged lateral flow through the A<sub>3</sub> horizon lies in the question: Is subterranean solidization or podzolization taking place? With the average pH values of the lateral percolates lying between 6.7 and 7.0, the podzolization process would undoubtedly be weak. On the other hand, with a high calcium status, such as that reported by Zobler and Kardos (12) for a similar soil, the solidization could hardly be expected to be strong. Further studies of the siliceous layer for the presence of readily soluble SiO<sub>2</sub>, which is described by Joffe (4) as a distinguishing attribute of the solodi, would aid in answering the question.

Furthermore, with increasing approach to the crest of the dunelike hills the accumulated lateral flow would become less and hence the internal soil climate

TABLE 8  
Average values of SiO<sub>2</sub>/R<sub>2</sub>O<sub>3</sub> ratios and pH

		FUNNEL DESIGNATION				
		A <sub>2</sub>	A <sub>3</sub>	B	Lat.	
1937-38	Cultivated	2.27 7.3	1.34 6.9	2.67 7.3	1.03 6.9	SiO <sub>2</sub> /R <sub>2</sub> O <sub>3</sub> pH
	Virgin	— —	4.16 6.7	3.18 7.3	2.84 7.0	SiO <sub>2</sub> /R <sub>2</sub> O <sub>3</sub> pH
1938-39	Cultivated	3.02 6.6	2.34 6.8	3.43 7.0	1.97 6.7	SiO <sub>2</sub> /R <sub>2</sub> O <sub>3</sub> pH
	Virgin	1.71 7.0	1.43 6.6	2.41 7.1	2.45 6.9	SiO <sub>2</sub> /R <sub>2</sub> O <sub>3</sub> pH
1939-40	Cultivated	2.14 6.9	2.05 6.9	2.40 7.2	2.27 7.0	SiO <sub>2</sub> /R <sub>2</sub> O <sub>3</sub> pH
	Virgin	2.65 6.9	3.61 6.8	2.34 7.2	2.84 6.9	SiO <sub>2</sub> /R <sub>2</sub> O <sub>3</sub> pH

more aridic. Added to this effect would be the lower moisture regime resulting from the blowing of snow from ridge-tops and their immediate southerly slopes by the strong southwesterly winds. As a net effect, the soil profiles on the ridges and immediately adjacent southerly slopes would tend to be true pedocals whereas the lower southerly slopes and interslopal basins would tend to be strongly degraded chernozems or weakly developed pedalfers of the prairie type.

#### *Agronomic aspects*

The most striking agronomic aspects revealed by the lysimeter data were the tremendous differences between virgin and cultivated areas in amounts of total solids, total nitrogen, nitrate nitrogen, and other primary nutrients which were transported through the profile. The numbers of pounds of material passing



through the various funnels, on an area basis, are shown in table 9. The differences arose particularly from the generally higher concentration of mineral and organic constituents in the drainage from the cultivated area. Specifically, the concentration of total nitrogen in the percolates of the cultivated area ranged from 5 to 15 p.p.m., whereas the percolates of the virgin area ranged from 2 to

TABLE 9  
*Vertical and lateral transport of soil constituents*

DRAINAGE SEASON AND LOCATION	FUNNEL DESIG- NATION	AVERAGE TOTAL LEACHINGS PER FUNNEL	TRANSLOCATED MATERIALS PER ACRE PER SEASON								
			Total solids	Total nitro- gen	SiO <sub>2</sub>	R <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	K <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>
		ml.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.
1937-38 Cultivated	A <sub>2</sub>	2,998	246.8	9.3	62.1	47.8	3.2	22.7	16.9	3.4	0.25
	A <sub>3</sub>	3,187	166.8	9.8	17.4	21.1	1.6	21.2	14.3	2.3	0.24
	B	7,089	411.2	16.5	47.0	31.0	3.0	45.7	37.8	1.5	0.42
	Lat.	36,970	959.6	50.7	119.4	211.0	43.7	105.5	72.3	8.0	0.90
1937-38 Virgin	A <sub>2</sub>	108*	—	—	—	—	—	—	—	—	—
	A <sub>3</sub>	11,882	306.4	4.1	113.5	50.1	10.6	13.5	23.2	1.9	2.41
	B	1,879	61.9	0.7	8.4	4.6	0.4	3.8	4.0	0.8	0.19
	Lat.	37,709	684.9	8.3	100.7	61.8	5.0	36.6	48.1	12.5	2.98
1938-39 Cultivated	A <sub>2</sub>	1,150	128.5	2.1	46.7	29.1	7.8	7.0	5.1	0.2	0.13
	A <sub>3</sub>	4,838	1,024.5	9.5	425.5	330.6	59.3	34.3	35.7	2.5	1.23
	B	4,855	839.9	7.4	310.5	170.4	44.9	35.4	28.2	3.2	0.47
	Lat.	108,990	8,605.7	70.8	3,244.3	3,016.8	597.8	292.9	350.0	30.8	12.97
1938-39 Virgin	A <sub>2</sub>	815	40.3	0.8	10.0	10.0	0.4	3.2	1.9	0.8	0.67
	A <sub>3</sub>	30,103	807.5	14.4	196.9	235.9	6.4	54.8	42.0	13.5	5.00
	B	3,043	118.8	1.7	33.6	24.1	1.2	9.2	5.7	1.4	0.78
	Lat.	162,745	3,204.6	58.7	877.2	622.4	36.0	264.8	236.1	23.9	31.60
1939-40 Cultivated	A <sub>2</sub>	1,831	224.4	5.1	69.4	60.0	13.6	13.8	31.4	6.2	0.48
	A <sub>3</sub>	4,144	599.5	10.9	197.1	178.8	44.0	28.8	61.9	13.2	1.40
	B	26,201	2,135.6	29.0	608.8	469.7	112.0	140.0	315.1	36.1	3.63
	Lat.	72,746	3,052.0	70.5	1,019.1	843.4	223.6	156.0	397.4	66.5	8.65
1939-40 Virgin	A <sub>2</sub>	1,252	34.9	0.9	9.5	6.4	0.8	3.3	5.0	1.4	0.20
	A <sub>3</sub>	16,875	371.8	8.6	131.2	66.2	11.7	34.7	88.7	6.2	1.58
	B	2,571	102.0	1.4	24.7	19.0	3.0	11.6	17.8	2.1	0.37
	Lat.	107,080	1,903.2	38.1	403.0	253.5	34.4	238.8	409.5	38.0	5.98

\* Insufficient for analysis.

3 p.p.m. The total solids were 2.5 to 5 times as concentrated in the percolates of the cultivated area. The nitrate-nitrogen values in the percolates of the cultivated area ranged from 20 p.p.m. to a trace whereas in the percolates of the virgin area the values ranged from 6 p.p.m. to a trace. Over 90 per cent of the percolates of the virgin area had less than 0.1 p.p.m. of NO<sub>3</sub>-N, whereas over 90

per cent of the percolates of the cultivated area had more than 0.1 p.p.m. of  $\text{NO}_3\text{-N}$ .

Since nitrogen is regarded as the principal limiting nutrient in the Palouse region, it was of particular interest to determine its fate in the soil. Sievers and Holtz (10) indicated that when virgin land was brought under cultivation considerable amounts of nitrogen were lost in a manner other than by crop removal. The lysimeter data indicate that not all of this loss is by surface erosion of organic matter; indeed, subterranean erosion of organic nitrogen may take place, and particularly nitrate-nitrogen may be leached from the slopes and concentrated in the interslopal basins. This latter loss does not occur to any appreciable extent from the virgin bunchgrass area because the ever-present root system together with the microflora constantly absorbs the free nitrate nitrogen almost as rapidly as it is formed. Although the pea-wheat rotation system used on the cultivated area was undoubtedly more conservative than a wheat-summer-fallow system, it was still not so conservative as the perennial bunchgrass. The data indicate that the root system of winter wheat after peas was not very conservative of nitrate nitrogen until some time in March. Persistence of nitrate-nitrogen levels in the percolates from the cultivated area during December, January, and February further indicated that nitrification may go on within the soil profile during these months. Assuming that nitrification is also going on within the virgin profile, the almost complete lack of nitrate in the percolates from the virgin area would indicate that the bunchgrass roots are actively absorbing nutrients throughout the winter. Collison (1) observed that apple roots continued to grow when soil temperatures were as low as  $36^\circ\text{F}$ . and possibly even closer to  $32^\circ\text{F}$ .

Of the primary mineral nutrients, the Ca, Mg, K, and P in the percolates tend to be associated with the total solids, which in turn are principally made up of the silica and sesquioxides. As the total solids increase, Ca, Mg, K, and P increase in the percolates of both cultivated and virgin areas. The K and P in the percolates of the virgin area increase, however, with the total solids at a faster rate than they do in the percolates of the cultivated area. This behavior is strongly indicative of a higher degree of circulation and hence of availability of the K and P in the virgin profile. The cropping systems on the cultivated area have undoubtedly been more exhaustive of K and P than of Ca and Mg and more exhaustive of P than of K. Hence, of the two nutrients, K and P, phosphorus is the more likely to become the next limiting element after nitrogen. Moreover, the reserve supply of potassium is about five times as great as that of the phosphorus, and the average losses of potassium through the lateral funnels are only three times as great as those of phosphorus.

The movement of Ca and Mg through the soil profile was much greater than that of K and P, and the concentration of K and P followed closely that of the total solids. From a comparison of the quantities of  $\text{SiO}_2$ , and  $\text{CaO}$ , and  $\text{MgO}$  it is readily apparent that a considerable fraction of the Ca and Mg must have moved as ions not associated with the colloidal clay. The solutions did contain appreciable quantities of bicarbonates which effervesced strongly when phenol-

disulfonic acid was added to the evaporated solutions in the nitrate-nitrogen determinations. The Ca and Mg were undoubtedly associated in some measure with this bicarbonate. The remainder of the Ca and Mg would then be associated with the organocolloids in the percolates of both the virgin and cultivated areas and, in addition, with the nitrate ion in the percolates of the cultivated area.

The loss on ignition, which comprised approximately one-sixth to one-half of the total solids, involved not only organic matter but also  $\text{NO}_3^-$ ,  $\text{HCO}_3^-$ , and water of hydration and constitution of the clay. No determinations of organic matter content were made, but in the virgin area percolates, at least, the nitrogen content indicated that a substantial fraction of the total solids was organic in character.

#### SUMMARY AND CONCLUSIONS

The Ebermayer type of lysimeter under the subhumid rainfall conditions of the Palouse country lent itself very well to elucidating the mode of the percolative processes in a soil profile on sloping land.

Probably the most striking indication was the tremendous amount of flow which took place parallel to the slope and 20 to 30 inches below the surface. This flow was intercepted in part by the  $A_2$  funnels and more completely by the lateral funnel.

The data further indicated that the pea-wheat rotation stimulated degradation of the soil profile not only from its surface erosion effects but also from the nature of the subsurface losses from the profile. The concentration of nitrogen in the percolating solutions from the cultivated (pea-wheat) area was two to six times as great as that in percolating solutions from the virgin (bunchgrass) area. During one year (1938-39) as much as 70.8 pounds of nitrogen per acre of funnel area moved past the lateral funnel of the cultivated area, together with 292.9 pounds of CaO, 350 pounds of MgO, 30.8 pounds of  $\text{K}_2\text{O}$ , and 12.97 pounds of  $\text{P}_2\text{O}_5$ . The N, P, and K thus transported are equivalent to more than 400 pounds nitrate of soda, 50 pounds muriate of potash, and 60 pounds normal superphosphate. This poundage of nutrients may be looked upon as moving downslope, within the soil profile, past a vertical area 55,000 feet long, slightly less than  $9\frac{1}{2}$  inches wide, and lying in a layer 24 to 34 inches below the surface. The loss of nutrients is significant and points to the possible future need of phosphatic fertilizers to satisfy the phosphorus requirements of a pea-wheat rotation. The pea crop may be expected to suffer first, since its root system is less extensive than that of wheat and it has a higher phosphorus requirement.

From the nature of the percolative processes as revealed by the lysimeters, it may be expected that the middle third of sloping areas would be more severely depleted than the upper or lower thirds because the upper third would be less subject to lateral flow and the lower third would be expected to receive some accumulations as the slope flattens toward the bottom.

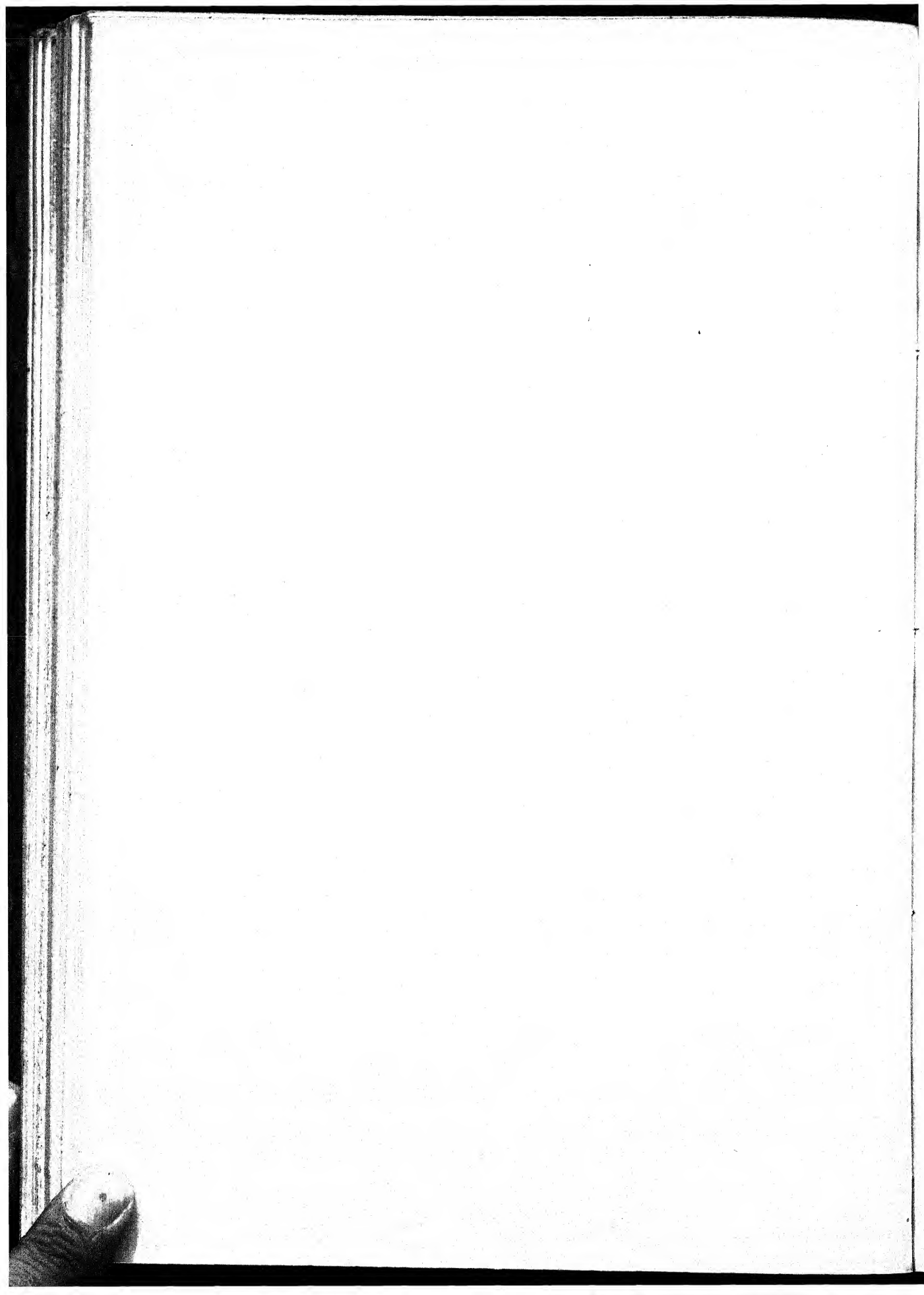
The hydrologic significance of the lysimeter data is difficult to evaluate, but

its ramifications can be visualized, for example, in the construction of terraces where the terrace channel may or may not intercept the subsurface storm flow or in the construction of surface runoff plots where no provision is made for the escape of the subsurface storm flow at the lower end of the plot.

The ultimate fate of the lateral or subsurface storm flow was not determined in this study. It should be of considerable interest to the hydrologist as well as to the pedologist, to the latter from the point of view of the suspended and soluble load of the flow, and to the former from the point of view of its contribution to stream flow patterns, flood peaks, and composition of streams.

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## CERTAIN ASPECTS OF THE MECHANISM OF AGGREGATE STABILITY IN WATER

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Aggregate stability is usually determined by wet-sieving, especially in water. The dipole and dielectric constant of the sieving liquid have been considered as important factors in determining stability of aggregates. Myers (13) observed a direct relationship between the dispersion of soil, on the one hand, and the dipole and dielectric constant of the dispersing liquids, on the other.

McHenry and Russell (12) found that the aggregate stability was highest in benzene, followed by ethyl alcohol and then by water. They explained their results in term of the relative solvating power of the liquids.

The extent of soil-air interface before wet-sieving has also been considered an important factor to the size distribution and stability of aggregates. Unequal swelling and the compressing of soil air within the capillaries, during the wetting process, are regarded as responsible for disintegration of air-dry clods (19). The relative aggregate stability in water of soils with varying moisture content, that is, at varying soil-air interface, has been interpreted by McHenry and Russell (12) on the basis of Russell's liquid dipole-cation-liquid dipole linkage hypothesis (14, 15, 16).

Henin (4, pp. 52-54) found that addition of alcohol to water decreased the disintegration of air-dry clods and that the quantity of aggregates larger than 0.2 mm. in diameter was correlated with the affinity of soils for the liquid rather than with the surface tension of the different alcohol-water mixtures.

The effect on aggregate stability of replacement of the soil-air interface by the soil-organic liquid interface, prior to wet-sieving in water, has been studied by Henin (5, 6), Myers (13), and McCalla (11). Henin observed that the pretreatment of soils with liquid hydrocarbons or halogen- and nitro-derivatives reduced the stability in water of aggregates of soils other than those rich in organic matter. He also found that soils which had no alkali ions in the exchange complex were protected against disintegration by water following pretreatment with alcohol, acetone, and ether-oxide.

Organic matter has long been known to be effective in producing stable granulation, but very little is known definitely about the nature and constituents of soil organic matter that bind the soil particles into stable aggregates. Kroth (9) refluxed aggregates from under bluegrass sod for 16 to 20 hours in Soxhlet with ethyl alcohol, acetone, and ether, and found that this method of extraction reduced the stability of Brookston aggregates to abrasion but had no effect on the stability of Miami aggregates.

<sup>1</sup> This paper is a part of the research materials of the author's doctorate thesis submitted to Cornell University in 1947. The author acknowledges his gratitude to M. B. Russell and R. Bradfield of Cornell University for their guidance and inspiration.

The object of the experiment described in this paper was to study certain physical aspects of the stability of aggregates to wetting liquid.

#### METHODS AND MATERIALS

Aggregate stability was determined by the method of McHenry and Russell (12). Soil samples for aggregate analysis were taken at a depth of 0 to 3 inches. The soil fraction that passed through a 4.7-mm. sieve but was retained by a 1.98-mm. sieve was air-dried and wet-sieved on a 0.90-mm. screen for determination of water-stable aggregates. Five grams of air-dry soil was put on the screen and allowed to soak in water for 1 minute. The screen was then vertically oscillated in the liquid by means of an electric motor at the rate of forty  $1\frac{1}{2}$  inch strokes per minute. The material left on the screen was transferred to an evaporating dish, dried at 105°C., and weighed. This weight minus the weight

TABLE 1  
*Dipole moment, dielectric constant, and solubility in water,  
of the liquids used in dispersion*

NAME OF LIQUID	DIELECTRIC CONSTANT*	DIPOLE MOMENT†	SOLUBILITY IN WATER‡ gm./100 ml.
Water.....	80.0	1.87	
Ethyl alcohol.....	25.7	1.69	$\alpha$
Acetaldehyde.....	21.6	2.72	$\alpha$
Acetone.....	21.4	2.84	$\alpha$
Ether.....	4.4	1.10	7.5
Benzene.....	2.3	0.00	0.082

\* International Critical Tables.

† *Trans. Faraday Soc.* 30, App., 1934.

‡ Hand Book of Chemistry and Physics, Chemical Rubber Publishing Co., Cleveland, Ohio.

of the primary particles was expressed, on the basis of the oven-dry weight of the soil, as the percentage of water-stable aggregates.

#### RESULTS AND DISCUSSION

##### *Qualitative estimate of relative degree of dispersion of soil in water and various organic liquids*

Soil samples taken from sod plots of various grasses and legumes grown on Dunkirk silt loam were used in this study. One gram of air-dry soil was taken in 10 ml. of liquid in a test tube. The test tube was corked and put inside an ice-cream container, which was then shaken end-over-end by hand 60 times as uniformly as possible. The shaking of different soil samples with the same liquid was done at one time. The liquids were water, ethyl alcohol, acetaldehyde, acetone, benzene, and ether. The dipole moment and dielectric constant of water and these organic liquids and the solubility of the liquids in water are given in

table 1. The relative degree of turbidity was noted qualitatively with the naked eye.

Water produced turbidity for all samples irrespective of the kind of crops grown. No dispersion of any one of the samples was apparent on shaking with ethyl alcohol. As for other liquids, such as acetaldehyde, acetone, benzene, and ether, the aggregates appeared to be almost stable, irrespective of the differences in the dipole moments or dielectric constants of the liquids (table 1). This finding is contrary to that of Myers (13), who observed that the relative degree of dispersion of soils in water and in various organic liquids was a function of the dipoles and dielectric constants of the liquids. An increase in the ionization or swelling of the soil colloids, which would tend to decrease cohesion and enhance the susceptibility of soil to dispersion, may not necessarily result from an increase in the dipole or dielectric constant of the wetting liquid. According to Winterkorn and Baver (18), the relationship between swelling and the dielectric properties of the liquid exists only if there is certain similarity in the molecular structure of the liquids. Henin (7) pointed out that liquids the polarity of which is due to an atom or a group of atoms without specific affinity for water, caused small lowering of cohesion of soil, which is a function of the dipole moment of the liquids; whereas liquids having groups of atoms with affinity for water bring about considerable lowering of cohesion. However, the influence of soil organic matter on the behavior of aggregates toward dispersion by water or by organic liquids, as will be discussed later, cannot be overlooked.

*Effect of organic-liquid pretreatment of soils on aggregate stability in water*

Soils treated with organic liquids and then air-dried were sieved in water to study the effect of such pretreatment on the stability of aggregates. Twenty-five grams of soil used in the previous experiment were allowed to soak in 100 ml. of ether in a  $\frac{1}{4}$ -liter bottle for 24 hours, after which the excess liquid was decanted.

The soils were then spread out until they were apparently air-dry. A portion of this air-dry soil was then immediately analyzed for water-stable aggregates. The remaining portion was treated with acetone in the same manner as it was with ether, prior to aggregate analysis. Because of the shortage of samples of these soils, different samples were used for pretreatment separately with acetone or ethyl alcohol. The results are given in table 2.

The data in table 2 show that aggregate stability was increased on pretreatment with ether for all samples except A<sub>1</sub>, which showed a decrease in aggregation. On the contrary, pretreatment with acetone of soils that were previously wetted with ether (soils A<sub>1</sub> to A<sub>4</sub>), lowered aggregate stability, except for soil A<sub>3</sub>, which showed an increase in aggregation. The pretreatment of soils directly with acetone (soils B<sub>1</sub> to B<sub>4</sub>) also decreased aggregate stability. Alcohol pretreatment brought about an increase in aggregation for all samples except D, which showed very low aggregation to start with.

It seems, in general, that pretreatment with alcohol or ether exerts a protective

action on the stability of aggregates, whereas acetone pretreatment causes a reduction in aggregate stability. It should be pointed out that soil D is cultivated and is very low in organic matter. The rest of the soils have been under sod crops or forests and have high organic matter contents.

An increase in aggregation by alcohol pretreatment, independent of the organic matter content of the soil, was also noted by Myers (13) and Henin (5, 6). But the results on the pretreatment with ether and acetone obtained by them and the author are rather conflicting. Certain points, however, have emerged from all these investigations: First, pretreatment of soils with organic liquids that are more or less highly soluble in water seems to stress an inverse relationship

TABLE 2

*Effect of ether, acetone, and ethyl alcohol pretreatments on percentage of water-stable aggregates (> 0.90 mm. diameter) of a certain soil fraction—1.98–4.7 mm. in diameter*

SAMPLE NUMBER	AGGREGATION			
	WATER*	ETHER†	ACETONE‡	ETHYL ALCOHOL‡
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
A <sub>1</sub>	80.1	76.3	71.6	—
A <sub>2</sub>	59.7	61.2	57.1	—
A <sub>3</sub>	65.2	74.9	69.1	—
A <sub>4</sub>	76.5	82.1	76.5	—
B <sub>1</sub>	41.5	—	36.0	—
B <sub>2</sub>	43.7	—	41.3	—
B <sub>3</sub>	47.9	—	46.2	—
B <sub>4</sub>	45.9	—	42.6	—
D	1.5	—	—	1.5
NP	15.0	—	—	18.9
OP	48.2	—	—	51.5
F	69.8	—	—	70.1

\* Average of four determinations.

† Average of two determinations.

‡ Average of three determinations.

between aggregate stability and the dipole moment of the liquids. Second, pretreatment of soils with organic liquids that are very slightly soluble or virtually insoluble in water has decreased aggregate stability for soils other than those rich in organic matter. The mechanism of the process in this case may not be hard to visualize. Since the attraction of the soil surface for water is usually more than it is for such organic compounds, the boundary between water and the organic liquid, which will tend to be concave toward the latter, will be driven toward the interior of the soil capillaries by the hydrostatic pressure difference set up by the curved surface (1). As a result, the organic liquid will be compressed between the fronts of water advancing from both ends of the capillary and will ultimately break through at the weakest points, causing disintegration of the aggregates in the same way as is done by explosion of entrapped air during

wetting. The breakdown of the aggregates will be a function of the soil organic matter content and also of the amount of organic liquid present during wet-sieving in water. The complete expulsion of the organic liquid by heating or otherwise, prior to wet-sieving in water, will eliminate its disruptive influence on aggregate stability, as was observed by Myers (13). The protective action of organic matter may be due to the nature of the organic exchange complex the make-up of which is different from that of the inorganic soil colloids and which may supply fairly strong linkages for combination with organic compounds. A thin film of organic liquid, strongly linked to soil surface through organic matter, will tend to lessen the spreading and destructive action of water, since water has a high cohesion and does not spread readily on such organic liquid (1). This may explain the postulate of Henin (7) that fixation of the organic liquid by soils is

TABLE 3

*Effect of alcohol extraction of soil organic matter on percentage of water-stable aggregates (>0.90 mm. diameter) of a certain soil fraction—1.98–4.7 mm. in diameter*

SAMPLE NUMBER	AGGREGATION		SAMPLE NUMBER	AGGREGATION	
	Water*	Soxhlet extraction*		Water†	Soxhlet extraction‡
	per cent	per cent		per cent	per cent
D <sub>1</sub>	6.6	2.1	D	1.5	2.1
D <sub>2</sub>	45.7	41.2	NP	15.0	22.5
O	21.7	24.1	OP	51.6	58.4
H	58.6	59.6	F	69.8	77.9
L	31.9	27.1			
M	37.9	34.7			

\* Average of two determinations.

† Average of four determinations.

‡ Average of three determinations.

the most probable cause of subsequent resistance of the sample to disintegration by water.

#### *Aggregate stability following alcohol extraction of soil organic matter*

Soil organic matter was extracted with 95 per cent alcohol in Soxhlet to determine whether the alcohol-soluble fraction contributed to any extent to the stability of aggregates. Different soil types were selected for this purpose: Dunkirk silt loam, cultivated (D<sub>1</sub>); Dunkirk silt loam under pasture (D<sub>2</sub>); Lyons silt loam, cultivated (L); Ontario silt loam, cultivated (O); Honeoye silt loam under forest (H); and Mardin silt loam under pasture (M).

Twenty-five grams of air-dry aggregates of 1.98–4.7 mm. diameter were put over a mass of cotton resting over the bottom of the Soxhlet. Another mass of cotton was put over the soil to dissipate the beating action of distilling alcohol. The extraction was carried on for 10 hours. After that, the soil was taken out of Soxhlet, air-dried for 24 hours, and then analyzed for water-stable aggregates. The data are given in table 3.



The data show that extraction of soils with alcohol had no uniform effect on the stability of aggregates: some soils increased and others decreased in aggregate stability after alcohol extraction. A similar observation was made by Kroth (9). It may be worth while to point out that the aggregates that passed through a 4.7-mm. sieve but were retained by a 1.98-mm. sieve were used for extraction with alcohol and that the aggregates were seen to disintegrate somewhat during extraction. It is possible that such disintegration might have produced secondary units of soil particles even smaller than 0.90-mm. in diameter. Since, following alcohol extraction and prior to wet-sieving in water, the aggregates were not passed again through the 1.98-mm. sieve to remove the smaller units, the results on aggregate stability determined prior to and after alcohol extraction cannot, therefore, be considered as exactly comparable.

Another set of experiments was started, however, in which the aggregates, after alcohol extraction, were passed through the 1.98-mm. sieve before aggregate stability was measured. In this experiment the variation due to soil type also was eliminated. The soil used was Dunkirk silt loam. Soil samples were taken from the following sites: forest stand (F), grass strip on the edge of a highway (OP), 1-year-old pasture (NP), and 10-year cultivated soil (D). Mechanical analysis of these various sites showed no appreciable variation in their clay content, which was about 17.4–18.9 per cent. But there was a wide variation in their carbon content, as follows: D (0.74 per cent), NP (1.31 per cent), OP (3.18 per cent), and F (3.60 per cent). The period of extraction was 24 hours. The results of aggregate stability, prior to and after alcohol extraction, are given in table 3.

Except soil D, which is very poor in organic matter, the aggregate stability of all soils was markedly increased after alcohol extraction. The alcohol turned yellow after extraction, and the color was most intense in the case of soils OP and F. Addition of the alcohol extracts and their subsequent evaporation and drying did not affect the aggregation of soil D at all. The increase in aggregate stability following Soxhlet extraction may be due to more effective dehydration of the aggregates, partly by heat and partly by alcohol, which will bring about more intimate orientation and consequently increase the resistance to disintegration by water.

#### *Effect of varying surface tension of water on stability of aggregates*

A study was undertaken to investigate the effect on aggregate stability of the lowering of surface tension of water by solid- and liquid-surface-active substances, as well as by thermal energy.

*Solid-surface-active substance.* A preliminary study with several different soil types showed that wet-sieving of the air-dry aggregates in two different concentrations of the wetting agents aerosol and tergitol did not exhibit any definite relationship between aggregate stability and lowering of the surface tension of water.

The experiment was, however, continued with soils which were of the same

texture but which were under different vegetation. The same soils, used in the previous experiment, were also used here. Tergitol, because of the presence of free alkali salts in its commercial solution, was excluded in this study. "Aerosol OT," which is dioctyl sodium sulfosuccinate and which can be obtained pure in the solid state, was used in this study. This substance, in very small amounts, lowers considerably the surface tension of water without affecting to any appreciable extent the viscosity of the liquid (2). Wet-sieving was done in the solutions of aerosol in water ranging in concentration from 0.001 to 1.0 per cent. Four determinations were made to measure the aggregate stability of each of the soil samples in water or any one of the aerosol concentration. The results are presented graphically in figure 1 for all soils except D, the aggregate stability of which, low as it was, was almost unaffected. The surface tension curve of water aerosol solution (2) is also given in figure 1.

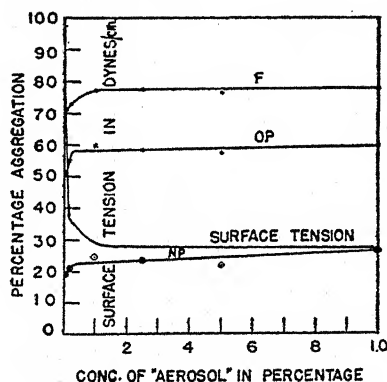


FIG. 1. EFFECTS OF INCREASING CONCENTRATION OF "AEROSOL" WETTING AGENT ON SURFACE TENSION OF WATER AND AGGREGATION OF SOIL

Dunkirk silt loam samples taken from forest stand (F), from grass strip on edge of a highway (OP), and from 1-year-old pasture (NP).

Figure 1 shows that the aggregate stability of soils NP, OP, and F increased somewhat with increasing concentration of aerosol solution up to a certain point. It may be worth while to point out that the maximum increase in aggregation occurred at the lowest concentration of aerosol solution, that is, at 0.001 per cent. The ignition loss at 105°C. of the soil moistened on the 0.90-mm. screen with either water or 1 per cent aerosol solution was almost the same, thus refuting the possibility of the increased aggregation's being due to absorption and retention of the wetting agent by the soil during wet-sieving and subsequent drying of the aggregates.

The increased aggregate stability in aerosol solutions may be due partly to the fact that lowering of the surface tension of water will slow down its capillary movement into the soil interstices (8) and allow the soil air to escape slowly from within the capillaries, thereby lessening the destructive action of entrapped air on the disintegration of aggregates. The results seem to contradict the popular

concept that anything that should increase wetting should also increase deterioration of structure (10). Bartell (3) points out the fallacy of the usual statement that liquids with the lowest surface tension give the highest degree of wetting of a solid and suggests that the question is, rather, one of the type of wetting under consideration.

*Liquid-surface-active substance.* Aggregate analysis was carried out in varying concentrations of alcohol in water to determine how alcohol, which, in addition to influencing the surface tension of water, has the ability to compete with water in the hydration of soil particles, would affect the stability of aggregates. A preliminary study with 22 soils, which were of different texture and contained different amounts of organic matter, showed that aggregate stability increased

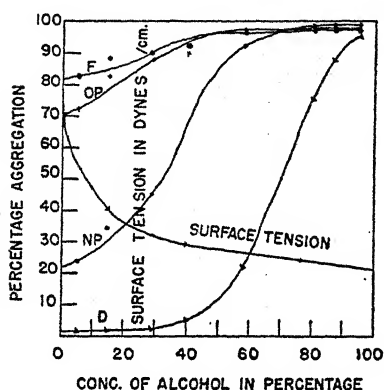


FIG. 2.

FIG. 2. EFFECTS OF INCREASING CONCENTRATION OF ALCOHOL ON SURFACE TENSION OF WATER AND AGGREGATION OF SOIL

Dunkirk silt loam samples taken from forest stand (F), from grass strip on edge of a highway (OP), from 1-year-old pasture (NP), and from 10-year cultivated soil (D).

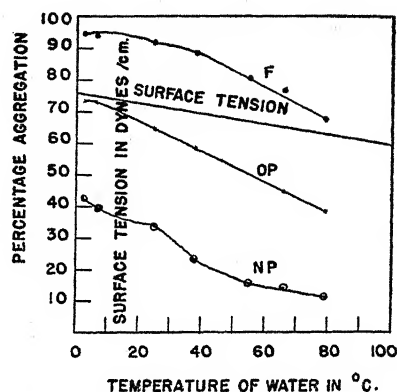


FIG. 3.

FIG. 3. EFFECTS OF INCREASING TEMPERATURE ON SURFACE TENSION OF WATER AND AGGREGATION OF SOIL

Dunkirk silt loam samples taken from forest stand (F), from grass strip on edge of a highway (OP), and from 1-year-old pasture (NP).

with increasing concentration of alcohol up to about 60 per cent. The order of aggregate stability of the different samples, as determined in pure water, was not maintained when analyzed in increasing concentration of alcohol.

In order to eliminate the variation due to soil type, the experiment was continued with the same soils used for study with wetting agents but sampled at a different period. Each determination was in duplicate and the duplicate determinations were each carried out in fresh solution of the respective alcohol concentration.

The results are presented graphically in figure 2, together with the surface-tension curve of alcohol-water mixtures. The data on aggregate analysis

represent the degree of aggregation of air-dry particles of 1.98–4.7 mm. diameter; the degree of aggregation means the percentage of particles <0.90-mm. in diameter aggregated into stable units >0.90-mm. in diameter.

Figure 2 shows that the aggregate stability of all soils except D increased with increasing alcohol concentration up to about 40–60 per cent alcohol. The aggregation of soil D, which is very poor in organic matter, on the contrary, showed no response until the concentration of alcohol has been raised to 40 per cent, after which there was a continual increase in aggregation with the increasing concentration of alcohol. The concentration of alcohol at which an increase in aggregation becomes apparent, or at which the maximum degree of aggregation occurs, is a function of the organic matter content of the soil. The difference in aggregation produced by varying alcohol-water mixtures is due to the difference in the relative solvating power of the mixtures rather than to the effect of surface tension, which dominates in the case of solid-surface-active substance but which is of minor importance in the case of liquid-surface-active substance such as alcohol. This solvating power of alcohol-water mixtures on aggregate stability is a function of the concentration of alcohol and also of the nature and amount of the colloidal surface of the aggregates.

*Thermal energy.* A study was also made to investigate how the lowering of the surface tension of water by thermal energy would effect the stability of aggregates. Prior to wet-sieving, the soil and water were brought to the same temperature. Soils used in the previous experiment, but sampled on a different date, were used in this study. The results of aggregate analysis, together with the surface tension curve of water, are presented graphically in figure 3 for all soils except D, the aggregation of which, low as it was, was almost unaffected by increasing temperature of water.

Aggregate stability decreased with increasing temperature for all soils (fig. 3), irrespective of their organic matter content. Wilson and Fisher (17) made a similar observation. The decrease may partly be explained by the fact that subjecting the soil to increasing temperature, which may remove the air adsorbed on the soil surface, tends to increase the wettability and decrease the stability of the aggregates.

#### SUMMARY

Experiments were conducted in the laboratory to investigate the mechanism of the stability of aggregates in water.

A qualitative study indicated that there was no relationship between dispersion of the soil, on the one hand, and the dipole and dielectric constants of the dispersing liquids, on the other.

Pretreatment of soils rich in organic matter with ether and alcohol generally increased the stability of aggregates in water, whereas acetone pretreatment decreased aggregation.

The stability of aggregates following extraction of soil organic matter with alcohol was determined in water.

Aggregate stability was determined in water to which different amounts of

solid- and liquid-surface-active substances and also of thermal energy were added. Solid-surface-active substance increased aggregate stability to some extent. Liquid-surface-active substance, on the other hand, increased aggregate stability with increasing concentration of the substance up to a certain point. Aggregate stability decreased with increasing addition of thermal energy to water, irrespective of the organic matter content of the soil.

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## CATION EQUILIBRIA IN PLANTS IN RELATION TO THE SOIL: II

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In an earlier paper<sup>2</sup> an attempt was made to establish the relation between the amounts of the four principal cations, Ca, Mg, Na, and K, in plants and in the soil substrate. The experiment led to the conclusion that for each of these cations the quantity present in the soil as well as its relation to the amounts of the other three cations is of great importance to cation absorption by the plant. In fact, it was possible to establish a quantitative relationship between plant and soil values.

In that experiment a sandy soil was used. Saturation of the adsorption complex with basic ions was low, only 30 per cent of its saturation capacity (*T*-value) being occupied by the four cations. The H-ion concentration was high, pH 4.3 in aqueous suspension. Large quantities of cations, in comparison to those already in the soil in exchangeable form, were added to provide ratios quite different from the original value. The original quantity of exchangeable Ca—6.7 m.e. in 100 gm. soil—was so large, however, that the added amounts could not increase the content very much. It was impossible, therefore, to study all the desired cation ratios, including low Ca values and high values for the other three ions.

In a second experiment, described elsewhere<sup>3</sup>, a soil of lower cation content was used. Its saturation capacity was only 11 per cent, 1.13 m.e. per 100 gm. soil being Ca. Addition of 13 m.e. Ca changed the ratio of exchangeable Ca to the sum of Mg, K, and Na from 2.1 to 24, in comparison with the ratio in the first experiment, which varied from 3.7 to 7.6.

In these two experiments the cations were added in the form of carbonates to effectuate an easy exchange with the H ions of the adsorption complex. These added cations plus those already present in solution and in exchangeable form, as determined by extraction of the soil with 0.1 *N* HCl, gave the cation values of the

<sup>1</sup> Dr. Th. B. van Itallie, who was killed in 1944 by war action, finished this article just before his death, but was unable to add a survey of literature on the subject. It is a great sorrow to know this publication to be the last one of this investigator, whose research has resulted in many excellent contributions to agricultural science.—P. BRUIN, Director.

EDITORS' NOTE: This paper, submitted in English, a language other than the author's native tongue, has been extensively edited. The meaning of some passages in the original version was not entirely clear, and as neither the edited manuscript nor the proof could, of course, be referred to the author, responsibility for any misinterpretation of these passages rests with the editors.

<sup>2</sup> Itallie, Th. B. van. Cation equilibria in plants in relation to the soil. *Soil Sci.* 46: 175-186. 1938.

<sup>3</sup> Itallie, Th. B. van. De chemische samenstelling van gewassen in verband met landbouwkundige vraagstukken, pp. 51-55. 's-Gravenhage Alg. Landsdrukkery. 1938.

soil which were considered in relation to the values found by analysis of young plants. It is evident that this relationship would have a much more solid basis if we had to deal with only one kind of cation in the soil, namely, that added to replace the H ions. To bring about this condition, we must first eliminate all cations present in the soil in exchangeable form and then add the cations we want as carbonates. This procedure also has the advantage that all possible ratios of the four cations in the soil can be established.

This paper deals with a series of experiments with a soil thus treated; that is, the bases were first replaced with H and then the desired cations were substituted. Wide differences in the manner in which the four principal cations were absorbed by the plant are discussed.

#### EXPERIMENTAL

The same soil was used throughout these experiments, in 1937, 1938, and 1939. A sandy soil from the northern part of the Netherlands, it contained 11 per cent humus and was low in basic ions; the pH was 4.2 in aqueous suspension; and 15 per cent of its total saturation capacity was occupied by bases. Cereal crops grown on this soil showed the typical symptoms of Mg deficiency so often seen on poor acid soils such as this. Additions of lime, as well as magnesia, have given very good results on this soil.

To remove the exchangeable bases, 0.1 N  $\text{H}_2\text{SO}_4$  was continuously percolated through 400 kgm. of the soil in a drained wooden tub. Fresh amounts of acid were poured on the soil for days, until the titration value of the acid no longer changed during percolation. The acid was then removed by percolating with water. Finally, distilled water was used until the sulfate reaction in the liquid flowing out became negative. The soil was then spread out to dry before use in the pot experiments. The humus looked somewhat peptized and was more distinctly separated from the sandy parts than before the treatment; the pH in aqueous solution had become 3.1.

Results of removal of the bases are shown in table 1. The exchangeable bases were determined by extraction at room temperature with 0.1 N HCl (1:20). By boiling with 10 per cent HCl (1:5) an indication was obtained as to the extent to which nonexchangeable bases had also been attacked by the acid treatment.

After extraction with 0.1 N HCl, the sum of the bases was found by titration with NaOH, and the single bases were determined by ordinary sensitive chemical methods. In the soil in which the bases were replaced by H, only Ca was found in appreciable quantity by the dilute acid extraction; of the Mg, K, and Na, only traces were left. It is safe to assume that approximately 90 per cent of the exchangeable bases were removed by the acid treatment. Subtracting the values for 0.1 N HCl extraction from those for 10 per cent HCl gives the cations present in nonexchangeable form. We see, then, that nonexchangeable K and Na were not released by the sulfuric acid and that but little Ca and Mg were removed. The analysis of the original soil by extraction with 0.1 N HCl served as the basis for the cation substitutions in all experiments.

The experiments were carried out in Mitscherlich culture vessels containing

4.5 kgm. of air-dried soil. The cations were always added as finely powdered carbonates, mixed with the dry soil before water was added and the vessels were filled. The necessary applications of nitrogen (0.5 m.e. per 100 gm. = 100 kgm. N per hectare) and phosphoric acid (0.2 m.e. = 200 kgm.  $P_2O_5$  per hectare) were made in solution. Some series received ammonium sulfate and monoammonium phosphate; and some, Ca or Mg nitrate. In the latter series the phosphate was in the mono-Ca or -K form. The quantities of Ca, Mg, or K so applied were deducted from the quantities supplied as carbonates. Oats were sown in all experiments. The soil was maintained at 50 per cent of its water-holding capacity at first, and at about 60 per cent later. The cultures were kept outdoors during the day and were exposed to heavy rainfall. At night they were placed in the greenhouse.

The sum of the four cations added to the acid-extracted soil was in every case

TABLE 1  
*Analysis of soil before and after treatment with 0.1 N  $H_2SO_4$*   
In m.e. per 100 gm. soil

CATIONS IN SOIL	EXTRACTION WITH 0.1 N HCl		BOILING WITH 10 PER CENT HCl	
	Before treatment	After treatment	Before treatment	After treatment
Sum of four bases	<u>3.2*</u>	0.3*	6.58†	3.04†
Ca	2.53	0.18	3.17	0.46
Mg	<u>0.30</u>	tr.	1.93	1.39
K	<u>0.25</u>	tr.	1.13	0.93
Na	<u>0.06</u>	tr.	0.35	0.26

\* Exchangeable, as determined by titration.

† Total, by calculation.

3.2 m.e. per 100 gm. soil (*S* value, see table 1) or a multiple of this figure. In a preliminary experiment a series with half the *S* value of cations was also tried, but this quantity proved too small, the pH of the soil becoming 3.5 and plant growth obviously impossible. The most important series in this experiment, those of 1937, as well as all those in the two following years fitted into a scheme in which the quantity of added Mg, on the one hand, and that of K and Na, in a fixed ratio, on the other, amounted to single and multiple quantities of the values in the original soil (underscored values in table 1); enough Ca was then added so that the total cations present amounted to the single, double, triple, or quadruple *S* value. Table 2 shows this scheme for the series with the single *S* value of cations added.

Besides the series with acid-extracted and base-substituted adsorption complex, some were also set up with the original soil without cation addition as well as with extra addition of one or two times the *S* value of the soil in different cation ratios.

It lies beyond the scope of this summarizing review to deal separately with the results of each year. The results on the uptake of cations were comparable in all

3 years and can, thus, be summarized. This increases the value of the results, because the conditions under which the plants grew, and the yields, were not so uniform in the three experiments. The growth and yield of the plants in different years must, therefore, be considered briefly before the cation percentages are discussed.

The first year the oats were sown late (April 10, 1937). The soil had only recently dried after the acid treatment, and its structure was poor. Weather conditions that spring were normal. The plants in the series to which the 1 *S* value of cations was added grew poorly, especially when N was supplied as  $\text{NH}_4$ . With the addition of the 2 *S* cation value the plants grew much better and gave almost the same yields as the comparable groups in the untreated soil. The plants were cut in the green stage on June 10, when the less vigorous plants

TABLE 2

*Experimental scheme—exchangeable cations present after addition to the acid-extracted soil*  
Series 1 *S* = 3.2 m.e. cations in 100 gm. soil

GROUP	Ca	Mg	K	Na	SUM
	m.e.*	m.e.	m.e.	m.e.	m.e.
1. { Original ratio Single original Mg value, original K + Na.....	2.55	0.30	0.25	0.10	3.2
2. Single original Mg value, 2 × original K + Na..	2.20	0.30	0.50	0.20	3.2
3. Single original Mg value, 3 × original K + Na..	1.85	0.30	0.75	0.30	3.2
4. Single original Mg value, 4 × original K + Na..	1.50	0.30	1.00	0.40	3.2
5. Double original Mg value, original K + Na.....	2.25	0.60	0.25	0.10	3.2
6. Double original Mg value, 2 × original K + Na..	1.90	0.60	0.50	0.20	3.2
7. Double original Mg value, 3 × original K + Na..	1.55	0.60	0.75	0.30	3.2
8. Double original Mg value, 4 × original K + Na..	1.20	0.60	1.00	0.40	3.2
9. Quadruple original Mg value, original K + Na..	0.60	1.20	1.00	0.40	3.2

\* M.e. = per 100 gm. soil.

showed their first panicles. The whole yield was weighed fresh. It was then oven-dried and ground fine for analysis.

The second year the oats were sown earlier (March 24). The acid-extracted soil, which had been stored for over a year, had a distinctly better structure than in the first year. After the seed sprouted, the weather was cold and windy. At harvest, on the same date as in the previous year, the plants were somewhat backward in their development. Remarkable, however, in this year, was the very good growth on the acid-extracted soil with the addition of 1 *S* cations. This growth surpassed that on the untreated soil and was only slightly less than that on the acid-extracted soil with addition of 2 *S* cations.

The third year the oats were sown on March 28. Weather conditions were very favorable, and the seed sprouted and grew quickly. On the whole, the plants showed a luxuriant growth. They were cut on May 26, about a fortnight

earlier than in the other years, in an earlier stage of growth and with a somewhat smaller yield of dry matter. Again, the acid-extracted soil to which 1 *S* was added gave a much smaller yield than the untreated soil. The yield of the untreated soil without cation addition was not greatly surpassed by the yields of the acid-extracted soils to which either 2 *S* or 3 *S* additions were made.

Table 3 shows a comparison of the yields of three groups in the three experimental years.

The dry weights obtained from the pots containing the original soil without addition of cations were nearly equal in the 3 years. It appears, therefore, that the differences in growth conditions in the three experiments had much more influence on the plants grown on the acid-extracted soil than on the untreated soil. The cause of this phenomenon has not been ascertained. Storage of the treated soil for a whole year after the first experiment, with the frost working on it in winter, improved the structure. Reduction phenomena at low pH values, which

TABLE 3  
*Relative yields of dry matter per pot of some groups in the three experiments (N as  $NH_4$ )*

GROUP	1937	1938	1939
Original soil, no cations added...	100 (= 15.3 gm.)	100 (= 16.5 gm.)	100 (= 14.8 gm.)
Acid-extracted soil with 1 <i>S</i> value of cations added .....	15	135	54
Acid-extracted soil with 2 <i>S</i> value of cations added .....	137	164	111

could be proved after the first experiment, probably disappeared in the following years when the soil structure was better. In the third year, however, a special test, in which the soil was kept wet for some months before the experiment was begun, failed to give any valuable indications, because the yield was about equal to that of the soil which was kept dry until the pots were filled. In the discussion of the phenomena of ion uptake by the plants grown on this soil with various cation ratios, these differences in yield from one year to another are not so important because, as already mentioned, the cation absorption followed the same pattern in every experiment.

#### DISCUSSION

##### *Cation-substituted soil compared with untreated soil*

Before the groups of soil with different cation ratios are considered, it is important to compare the cation contents of plants grown on the treated and the untreated soil. Table 4 gives the following data: first, for the acid-extracted soil with 1 *S* value of cations added in the original ratio in comparison with those for the original soil with no addition; and second, for the acid-extracted soil with 2 *S* value of cations added in varying ratios of Ca:(K + Na) in comparison with those for the original soil with 1 *S* value added in the same way.



As was shown in table 3, growth on soil treated with acid and afterward saturated with carbonates to the value of the original soil varied from year to year much more than did that on the original soil. Data for these groups are therefore given for 2 years.<sup>4</sup> In all three experimental years the plants on the original soil were much more vigorous in appearance; even in the second year, when the treated soil gave a higher yield, the plants on the original soil showed a more abundant growth, although they remained shorter. The plants on the rebuilt soil suggested a lower degree of cation saturation of the soil than did those on the original soil. This is confirmed by the soil analysis in table 1 and even more strongly by the analysis of the plants.

The cation contents of the plants in table 4 show, for the original soil with no additions, only small variations in the 2 years; for the acid-extracted soil + 1 *S* value, the low yield in the third year may account for the somewhat higher contents of Ca, Mg, and K. The striking difference between rebuilt and original soil in both years lay in the Ca content, indicating that in the original soil much more Ca was available for the plants than in the treated soil. In accord with this hypothesis, the soil analysis (table 1) showed  $3.17 - 0.46 = 2.71$  m.e. of total Ca against  $2.53 - 0.18 = 2.35$  m.e. of exchangeable Ca removed by the acid treatments. It seems probable that part of the Ca afterward added as carbonate made up for the loss of the nonexchangeable Ca, and hence the degree of saturation of the adsorption complex and the pH value of the soil<sup>5</sup> were lower. Less Ca was available for the plant, and the ratio of Ca to the other cations—especially the monovalent ions—in the medium was smaller, resulting in a smaller Ca uptake.

The soil analysis also indicates a greater loss of total Mg than of exchangeable Mg due to the acid treatment. One would expect a higher Mg content in the plants on the original soil. The cation contents do not indicate so marked a difference in Mg available to the plant as in the case of Ca, but in the other groups shown in table 4 they point in this same direction. We must remember, too, that the original untreated soil was much too acid and too deficient in Mg to produce plants with a normal Mg content. On the original soil without Mg addition the plants in the pot experiments as well as those in the field trials showed marked symptoms of Mg deficiency. These symptoms were more pronounced in plants with otherwise good growth than in plants already checked in growth by other factors, as in the case of the treated soil.

With the doubling of the cation content of the soil, in the original ratio, the pH value of the acid-extracted soil in the third experiment rose from 3.8 to 4.3. In the original soil the addition of an extra amount of carbonates to the *S* value of 6.4 m.e. changed the pH in the soil suspension from 4.0 to 4.6. In both cases, with the increasing base-saturation of the soil, a much higher yield was recorded.

The double cation addition in the original ratio to the acid-extracted soil raised the cation contents of the plants, except for Na. On the other hand,

<sup>4</sup> In the first year the yield of this group was too small for reliable analysis.

<sup>5</sup> In the first and second experiments no difference in pH between treated and untreated soil was observed.

addition to the original soil of the same amount of cations already present in exchangeable form marked an increase in the Mg, K, and Na contents and a decrease in the Ca content of the plants.

This again indicates the difference in availability of the cations between the treated and the untreated soil. In this series with 6.4 m.e. of exchangeable cations, when Ca was partly replaced by K and Na (table 4), the produce of both soils showed a decrease in Ca, Mg, and Na content and an increase in K content.

TABLE 4

*Results with acid-extracted soil after addition of 1 S and 2 S values of cations and with original soil without added cations and with 1 S value of cations added (N as  $NH_4$ )*

EXPERI- MENTAL YEAR	EXCHANGEABLE CATIONS PER 100 GM. SOIL					SOIL pH	YIELD OF DRY MATTER PER POT	CATION CONTENT OF PLANTS*					
	Total	Ca	Mg	K	Na			Ca	Mg	K	Na	Sum	
	m.e.	m.e.	m.e.	m.e.	m.e.			gm.	m.e.	m.e.	m.e.	m.e.	m.e.
	<i>Acid-extracted soil + 1 S value of cation</i>												
II	3.2	2.55	0.3	0.25	0.1	4.1	22.3	10.5	10	41	25.5	87	
III	3.2	2.55	0.3	0.25	0.1	3.8	7.95	16.5	13.5	71	25.5	126.5	
<i>Acid-extracted soil + 2 S value of cation</i>													
III	6.4	5.1	0.6	0.5	0.2	4.3	16.4	19.5	18	101	12.5	151	
III	6.4	4.4	0.6	1.0	0.4	4.3	16.0	12	14.5	121	5	152.5	
III	6.4	3.7	0.6	1.5	0.6	4.5	14.0	13	13	134	10.5	170.5	
<i>Original soil (no additions of cations)</i>													
II	3.2	2.55	0.3	0.25	0.1	4.1	16.5	41	18.5	54.5	22.5	136.5	
III	3.2	2.55	0.3	0.25	0.1	4.0	14.8	42	13	65.5	21.5	142	
<i>Original soil + 1 S value of cations</i>													
III	6.4	5.1	0.6	0.5	0.2	4.6	25.3	30	22	76.5	24	152.5	
III	6.4	4.75	0.6	0.75	0.3	4.8	23.3	22	17.5	113.5	23.5	176.5	
III	6.4	4.4	0.6	1.0	0.4	4.7	25.1	18.5	16.5	142.5	21.5	199	
III	6.4	4.05	0.6	1.25	0.5	5.0	24.1	16	15	153.5	19.5	204.5	

\* Per 100 gm. dry matter.

Except for Na, the composition of the plants with increasing additions of mono-valent ions became more nearly similar for both soils. As is discussed more fully later, this was due to the growing influence of K on the other cations. With increasing additions of K this effect more or less wiped out the original difference between the treated and the untreated soil.

In the other series, although conditions of plant growth after acid-extraction of the soil and replacement with other cations were not exactly the same as on the original soil, the variations in plant composition followed the same course. *The facts established in the experiments with the untreated soil can probably, therefore, be applied to normal soil conditions.*

*Varying cation ratios added to acid-extracted soil*

In the third experimental year the scheme of cation addition, in varying ratios, to the acid-extracted soil, as shown in table 2, was applied. Dry weights and cation contents of plants are given in table 5.

A striking feature of these data is the tendency toward decreasing yields with the increasing replacement of Ca by K and Na, beginning with the second or third increment; whether Mg was added in the original or twice the original quantity did not influence the yield. When, however, with the highest K + Na addition, the amount of Mg was again doubled, a further decrease in yield was noted. As has been mentioned, the yields in this series were low in comparison with those on the untreated soil (table 3). The plants in all groups showed poor growth; they looked stiff and spiky with light-colored narrow leaves. It is very

TABLE 5

*Dry weights and cation contents of plants on acid-extracted soil with addition of 3.2 m.e. cations in varying ratios (N as  $NH_4$ ; third experimental year)*

EXCHANGEABLE CATIONS PER 100 GM. SOIL				YIELD OF DRY MATTER PER POT	CATION CONTENT OF PLANTS*				
Ca	Mg	K	Na		Ca	Mg	K	Na	Sum
<i>m.e.</i>	<i>m.e.</i>	<i>m.e.</i>	<i>m.e.</i>	<i>gm.</i>	<i>m.e.</i>	<i>m.e.</i>	<i>m.e.</i>	<i>m.e.</i>	<i>m.e.</i>
2.55	0.3†	0.25	0.1	7.95	16.5	13.5	71.5	25.5	127
2.20	0.3	0.50	0.2	7.45	8	11.5	84.5	20.5	124.5
1.85	0.3	0.75	0.3	6.85	9	11.5	89	21.5	131
1.50	0.3	1.00	0.4	4.45	7	10	88	16	121
2.25	0.6‡	0.25	0.1	6.65	11	16	68.5	26.5	122
1.90	0.6	0.50	0.2	8.3	7	14.5	82	17	120.5
1.55	0.6	0.75	0.3	7.0	7	13.5	84	20.5	125
1.20	0.6	1.00	0.4	4.45	6.5	14	87	25	132.5
0.60	1.2§	1.00	0.4	3.25	5	17	75	29	126

\* Per 100 gm. dry matter.

† Original Mg value.

‡ Mg 2 × original value.

§ Mg 4 × original value.

likely that the poor growth and unhealthy appearance of the plants as well as the decreasing yields were due to Ca deficiency. In the last group receiving the fourfold Mg combined with the greatest amount of K and Na, the leaves showed typical yellow stripes common on plants grown in a culture medium very deficient in Ca but with enough Mg. The course of the steadily decreasing Ca contents of the plants in this series to a minimum value of 5 m.e. for the last group confirmed this hypothesis.

In the first four groups of this series, Mg was also at a minimum. With the development of the third and fourth leaves, the plants in the group with 0.3 m.e. Mg, like the otherwise much more vigorous plants on the original soil without cation addition, showed the typical shifting of chlorophyll color (yellow dots in green field or *vice versa*) in the leaves which is characteristic of Mg deficiency in

the plant. This phenomenon was aggravated with increasing alkali-ion additions but did not appear with the double and quadruple Mg additions. In this case also, the Mg contents of the plants were entirely compatible with this abnormal symptom in plant growth.

The K content of the plant, in general, increased with increasing additions of this ion. It was somewhat affected by the amount of Mg added; that is, with a higher proportion of magnesium in the Ca + Mg addition, the K content was lower.

The changes in Na content were undoubtedly the most curious feature in these experiments. Although K and Na, always in a fixed ratio to each other, were adjusted to Ca and Mg, the varying quantities of K and Na that made up the ratio produced very different ratios of K and Na in the plants. Despite the fact that Na was added in multiple increments, the plant content decreased in the first four groups. With the double Mg addition, the same alkali additions produced first a decrease and then an increase in the Na content. When K in the plant was depressed by the fourfold Mg addition, Na was again unaffected.

The scheme of the following series was similar to that of the first series, but the quantity of cations added to the acid-extracted soil was double and triple that in the original soil. The data on these two series are combined in table 6 (see also table 4).

With the addition of greater quantities of carbonates, the degree of saturation of the soil naturally rose. The pH value for the first group in each of the three series with 3.2, 6.4, and 9.6 m.e. of cations in aqueous suspension was found to be 3.8, 4.3, and 4.9, respectively. In view of the very low pH value for the second series, one would expect a still better growth for the third series with a more normal pH. The better growth for both these series, in comparison to the first series, was undoubtedly due, however, to the further cation saturation of the acid-extracted soil. The plants of the first groups of both the second and third series looked healthy and normal. The maximum yield on the original soil to which 3.2 m.e. of cations was added (pH of the soil 4.6) was not reached, but we do not believe cation deficiency or unfavorable ratio was responsible.

Again, the unfavorable effect of increasing replacements of Ca by K and Na in both series, however, was certainly due to Ca deficiency, although the exchangeable Ca in the soil of the third series with the highest alkali addition (4.5 and 3.6 m.e.), for example, was much higher than the value of 2.55 of the original soil without addition. Growth responses and cation contents of the plants demonstrated this fact clearly. Mg-deficiency symptoms were recorded for the groups with 0.6 m.e. Mg and 2.0 m.e. K and for the group with 0.9 m.e. Mg and 3.0 m.e. K. Yellow stripes, probably due to Ca deficiency, were noted in the groups with 2.4 and 1.2 m.e. Ca and 2.0 m.e. K and in the groups with 3.6 and 1.8 m.e. Ca and 3.0 m.e. K. The cation contents of the plants were again fully in agreement with these symptoms. The Ca contents in these series began on a somewhat higher level than with the same ratio in the 1 S series but again showed a marked drop under the influence of decreasing Ca and increasing alkali in the soil. The lowest Ca content probably ever recorded in oat plants was

found in the last group of the series with 9.6 m.e. (3 m.e. Ca per 100 gm. dry matter equals 0.08 per cent CaO). The effect of replacement of Ca by Mg, although clearly evident, was again much less pronounced than the effect of replacement of Ca by K and Na. The Mg contents showed the same trend as

TABLE 6

*Dry weights and cation contents of plants on acid-extracted soil with additions of 6.4 and 9.6 m.e. cations in varying ratios (N as  $NH_4$ ; third experimental year)*

EXCHANGEABLE CATIONS PER 100 GM. SOIL				YIELD OF DRY MATTER PER POT	CATION CONTENT OF PLANTS*				
Ca	Mg	K	Na		Ca	Mg	K	Na	Sum
m.e.	m.e.	m.e.	m.e.	gm.	m.e.	m.e.	m.e.	m.e.	m.e.
<i>6.4 m.e. cations added</i>									
5.1	0.6†	0.5	0.2	16.4	19.5	18	101	12.5	151
4.4	0.6	1.0	0.4	16.0	12	14.5	121	5	152.5
3.7	0.6	1.5	0.6	14.0	13	13	134	10.5	170.5
3.0	0.6	2.0	0.8	8.25	...‡	—	—	—	—
4.5	1.2§	0.5	0.2	17.2	17	21	102	12	152
3.8	1.2	1.0	0.4	16.25	14.5	18	123	6	161.5
3.1	1.2	1.5	0.6	13.1	8	13	136	10.5	167.5
2.4	1.2	2.0	0.8	8.4	8	15	138	14	175
1.2	2.4	2.0	0.8	5.95	5.5	18	118	11.5	153
<i>9.6 m.e. cations added</i>									
7.65	0.9¶	0.75	0.3	16.5	19.5	15	129	5	168.5
6.6	0.9	1.5	0.6	10.8	12	13	156.5	8	189.5
5.55	0.9	2.25	0.9	10.3	9	13.5	158	16.5	197
4.5	0.9	3.0	1.2	7.4	7.5	12.5	147	25.5	192.5
6.75	1.8**	0.75	0.3	17.5	15.5	18	129	4	166.5
5.7	1.8	1.5	0.6	13.3	10	15.5	150	7	182.5
4.65	1.8	2.25	0.9	10.4	8.5	15	162	16.5	202
3.6	1.8	3.0	1.2	8.15	5.5	12	132	21.5	171
1.8	3.6††	3.0	1.2	3.45	3	15	118.5	18.5	155

\* Per 100 gm. dry matter.

† Mg 2 × original value.

‡ Sample lost.

§ Mg 4 × original value.

|| Mg 8 × original value.

¶ Mg 3 × original value.

\*\* Mg 6 × original value.

†† Mg 12 × original value.

before; in both series, the Mg content remained almost constant when Mg and K + Na were changed in the same ratio.

In the series with 6.4 m.e. cations, the K contents of the plants increased regularly with increasing additions of the alkali carbonates. Reversing the Ca:Mg ratio of 2:1 to 1:2 in the last groups caused a depression in the K content, as in the other two series. In the series with 9.6 m.e., on the other hand, the



highest alkali addition of 3.0 m.e. K and 1.2 m.e. Na caused a distinct decrease in K content of the plant after the initial increase. Again, it is clearly the very curious mutual influence of K and Na which appears here.

Data in tables 5 and 6 on the relations of the uptake of Na and K show that, for corresponding additions of these ions in the various series, the larger the total amount of cations in the soil, the higher the K content and the lower the Na content of the plants. For example, when 1.0 m.e. K and 0.4 m.e. Na were added to the soil in series 1 (with 1.8 m.e. Ca + Mg), in series 2 (with 5 m.e. Ca + Mg), and, by interpolation, in series 3 (with 8.2 m.e. Ca + Mg) the ratios and alkali-ion contents were as follows:

	Ca + Mg K + Na IN SOIL	M.E. K IN PLANT	M.E. Na IN PLANT
Series 1.....	1.3	87.5	20.5
Series 2.....	3.6	122	5.5
Series 3.....	5.9	138	4

An increasing uptake of K by the plant, when Ca carbonate was added, was often found, especially at low pH values, where the exchange of H ions by Ca ions in the adsorption complex seemed to increase the availability of K to the plant. Whether Na and Mg also can profit by the addition of Ca as the carbonate depends probably on the amount of K present, because this factor ultimately regulates the uptake of the other two ions.

In each of the three series with single, double, and triple total cation additions, mutual replacement of Ca, Mg, and Na by K occurred in the plant to a greater or less degree, the total cation uptake tending to increase with increasing additions of alkali. Between series, no such mutual replacement was found, and the higher K level when the cation content of the soil was raised from 3.2 to 6.4 m.e. and from 6.4 to 9.6 resulted also in higher total cation contents.

When only small quantities of alkali carbonates were added to the soil, the Na content of the plants evidently depended chiefly on the amount of K taken up, and not on the amount of Na added. Up to the fourth increment, the Na content decreased, and the K content rose noticeably. On the other hand, in the first series, with the fourth increment of alkali carbonates and the fourfold Mg addition, the K content was distinctly lowered and the Na content again became higher. With the larger additions, however, the Na content of the plants rose steadily, independent of the K uptake; the extra Mg addition slightly depressed the Na content as it did the K. It is likely, in view of the results of our previous experiments<sup>6</sup>, that, for the highest additions, the tables were turned and Na depressed the K uptake somewhat.

In the three experimental series just discussed, the alkali ions have a dominant position, insofar as the ratios to Ca + Mg vary from 1:1 to 16:1, expressed in terms of the original value of the soil (see table 1).

<sup>6</sup> See footnotes 2 and 3.

Next to be considered are some groups with ratios smaller than 1:1, thus giving Ca and Mg and, curiously enough, also Na, a chance to dominate instead of K.

The first two such groups in table 7 show the effect of doubling the total cations in the soil without raising the Mg, K, or Na addition; the whole of the extra 3.2 m.e. addition in group 2 is in the form of Ca as the carbonate. The Ca and Mg uptake of the plants was increased to the same degree, whereas the K content remained the same and the Na content was somewhat lowered.<sup>7</sup> Comparison of groups 2 and 3 in table 7<sup>8</sup> shows clearly that with the addition of the extra 3.2 m.e. in the same ratio as the first 3.2 m.e., the uptake of Ca and Mg was depressed by the presence of the double amount of K, although Mg also was doubled. The same effect of doubling the cation content of the soil by Ca addition can be seen by comparing groups 3 and 4. This addition of Ca as the carbo-

TABLE 7

*Dry weights and cation contents of plants on soil with large calcium and small alkali additions (N as NH<sub>4</sub>; first and second experimental years)*

GROUP	YEAR	EXCHANGEABLE CATIONS PER 100 GM. SOIL					YIELD OF DRY MATTER PER POT	CATION CONTENT OF PLANTS*				
		Total	Ca	Mg	K	Na		Ca	Mg	K	Na	Sum
		m.e.	m.e.	m.e.	m.e.	m.e.		m.e.	m.e.	m.e.	m.e.	m.e.
1	II	3.2	2.55	0.3	0.25	0.1	22.3	10.5	10	41	25.5	87
2	II	6.4	5.75	0.3	0.25	0.1	21.5	22	22.5	41	21.5	106
3	II	6.4	5.1	0.6	0.5	0.2	27.0	16	17	61	20.5	114.5
4	II	12.8	11.5	0.6	0.5	0.2	22.5	26.5	20.5	75.5	30	152.5
5	II	6.4	4.4	0.6	1.0	0.4	27.9	13.5	12.5	97.5	9.5	133
6	II	12.8	10.8	0.6	1.0	0.4	23.8	19.5	13.5	127.5	12.5	173
7	I	6.4	6.4	—	—	—	6.8	42	19.5	20.5	62	144

\* Per 100 gm. dry matter.

nate raised the pH of the soil from 4.3 to 5.3 and increased the availability of all four cations. The relatively small proportion of K in the 12.8 m.e. of added cations could not mask the greater availability of the three other ions. The increase of Na was especially marked. As in the series previously mentioned, plants much richer in total cation content were produced on the highly saturated soil. When groups 5 and 6 of table 7 were compared, the same doubling of cation addition was noted but the level of K and Na ions was higher. Again the plant

<sup>7</sup> In our opinion, the author has overlooked the fact that the conditions in some experiments dealing with soils given very small potassium additions of 0.25 and 0.5 m.e. per 100 gm. (see tables 7, 8, and 10) were not suitable to detect differences in the intake of this element by the plants. In these cases, almost all the potassium added to the soil has been taken up by the plants. For instance, in the experiment reported in table 7,  $45 \times 0.25 = 11.25$  m.e. K was present in each pot, whereas the plants took up  $41 \times 0.223 = 9.14$  m.e.; besides, a certain amount was present in the roots. To draw correct conclusions from the experiments with low potassium additions the plants should have been harvested at an earlier stage. We did not, however, change the original text of our late colleague (see footnote 1).—P. BRUIN.

<sup>8</sup> This effect is shown more clearly in the third experimental year (first groups of tables 5 and 6).

content of all four cations was increased, but the increase in Ca, Mg, and Na was on a smaller scale than before, because of the greater influence of K.

Finally, group 7 in table 7 gives the composition of the plants in the first experimental year for a group receiving an addition of Ca as the carbonate only. With the addition of 3.2 m.e. Ca to the acid-extracted soil, practically no plant growth occurred, but with the double amount a small yield of yellow crumpled plants, probably with extreme K deficiency, was produced. The composition of these plants was marked by a very low K and an extraordinarily high Na content; the Mg content, on the other hand, was quite normal, and the Ca content,

TABLE 8

*Dry weights and cation contents of plants on acid-extracted and original soil with mutual replacement of calcium by magnesium (N as  $NH_4$ ; second experimental year)*

EXCHANGEABLE CATIONS PER 100 GM. SOIL					RATIO Ca:Mg	YIELD OF DRY MATTER PER POT	CATION CONTENT OF PLANTS*				
Total	Ca	Mg	K	Na			Ca	Mg	K	Na	Sum
m.e.	m.e.	m.e.	m.e.	m.e.		gm.	m.e.	m.e.	m.e.	m.e.	m.e.
<i>Acid-extracted soil with 2 S value of cations</i>											
6.4	5.4	0.3	0.5	0.2	18	29.1	17.5	14	60	20.5	112
6.4	5.1	0.6	0.5	0.2	8.5	27.0	16	17	61	20.5	114.5
6.4	4.5	1.2	0.5	0.2	3.75	25.8	14.5	20	67	21.5	123
6.4	2.7	3.0	0.5	0.2	0.9	28.9	8	26	58.5	19	111.5
<i>Acid-extracted soil with 4 S value of cations</i>											
12.8	10.8	0.6	1.0	0.4	18	23.8	19.5	13.5	127.5	12.5	173
12.8	10.2	1.2	1.0	0.4	8.5	21.4	19.5	17.5	140.5	12.5	190
12.8	5.4	6.0	1.0	0.4	0.9	17.6	8	26	112	17	163
<i>Original soil with 2 S value of cations added</i>											
9.6	8.25	0.3	0.75	0.3	27.5	33.7	24.5	11.5	76	23.5	135.5
9.6	7.65	0.9	0.75	0.3	8.5	28.5	24.5	22	81.5	26.5	154.5
9.6	2.85	5.7	0.75	0.3	0.5	30.4	9	39	78	23	149

\* Per 100 gm. dry matter.

as would be expected, was very high. The plant composition and the soil analysis after treatment, given in table 1, indicate that the K for plant growth, in this case, was not readily supplied from the large reserve (0.93 m.e.) of K in non-exchangeable form in the soil. It is curious, however, that three times as much Na as K was taken up by the plant, although no appreciable amount of Na in exchangeable form was left in the soil after the acid treatment and only little was present in nonexchangeable form (0.26 m.e.). Mg, also could evidently be taken up in sufficient amount when K did not interfere.

All the examples suggest the very important part played by the K ion in the uptake of the other three cations.

The mutual influence of Ca and Mg ions in the soil on the uptake of cations is brought out in table 8. Here data on two series with double and quadruple S

values of cations added to the acid-extracted soil are compared with one series of the original soil with extra addition of the *S* value. The alkali carbonate additions remained constant throughout each series.

There was a tendency toward a small depression in yields when Ca was replaced partly by Mg; no abnormal growth symptoms were noted, however, even when more Mg than Ca was added to the soil. The changes in Ca and Mg contents of the plants were quite normal: increasing Mg and decreasing Ca contents when more Mg and less Ca were added to the soil. With  $8\frac{1}{2}$  times more Ca than Mg added, plant contents of both were about the same; with equal amounts of both ions added, the Mg content was about three times that of calcium. There was good agreement in the changes in the values for the treated and the original soil. It seemed that the lower Mg additions caused a small increase in the K content of the plants; the large addition of Mg, however, effected a slight lowering of the K content, as in the third-year series. Only in the series with the fourfold cation value was more Na taken up when the K content decreased. From this series it can be concluded, in agreement with our previous experiments on cation equilibria, that the relation between the uptake of the two bivalent cations Mg and Ca is less complicated than that between the two monovalent alkali ions.

#### *Comparison of ammonia and nitrate as sources of nitrogen*

The experiments so far described all had the same basic treatments of  $\text{NH}_4$  as the sulfate and phosphate, thus receiving no nitrate. Nitrate series were also included in the general plan, however, because of the well-known fact that the form of nitrogen, especially in culture mediums with low pH, has a strong influence on the ion uptake. The necessity of supplying a small portion of the added cations, mostly Ca, in the nitrate series in the form of nitrate and phosphate instead of wholly as carbonate has already been mentioned.

As was to be expected from our previous experiments and in accordance with many references in the literature, the groups receiving nitrate always produced better plant growth than those receiving  $\text{NH}_4$ , the difference being especially large when the yield with  $\text{NH}_4$  fertilization was low. In the first year, for example, when the cations were added to the acid-extracted soil in the amount and ratio of the original soil, the yield with  $\text{NH}_4$  was only 2.25 gm. of dry matter as compared with 17.05 gm. with nitrate. In the second year, when yields were much better (see table 3), the same group yielded 22.3 gm. with  $\text{NH}_4$  and 24.7 gm., only slightly more, with nitrate. At the close of the experiment, the pH values for these groups in both years varied between 3.8 and 4.0; no more alkaline reaction of the soil due to the nitrate could be detected. On the other hand, nitrification of  $\text{NH}_4$  on the acid-extracted soil at these low pH values could not be expected. It is probable, therefore, that the plants under otherwise similar conditions took up either  $\text{NH}_4$  or nitrate. In the first year the nitrate-treated plants, as a whole, were somewhat richer in Ca and Mg and somewhat poorer in K and Na than were the  $\text{NH}_4$ -treated plants; but in view of the contradictory and more reliable results of the second year, these differences cannot be generalized.



In our experiments on Mg deficiency, a typical ion-balance problem, we frequently found, under nitrate fertilization, normal healthy plants with the same Ca and Mg content as plants fertilized with  $\text{NH}_4$ , but the  $\text{NH}_4$  produced severe symptoms of Mg deficiency and sometimes also of Ca deficiency. This led to the hypothesis that when  $\text{NH}_4$  is taken up, the plants need more Ca and Mg as protection against a strong H-ion invasion, which does not occur with nitrate source.

A similar explanation might possibly account for the results of the following series, in which  $\text{NH}_4$  and nitrate are compared in the second year when increasing amounts of alkali carbonates replaced the Ca. Almost the same series, with only  $\text{NH}_4$  included, in the experiments of the third year has already been discussed (table 6). The yield figures in table 9 show the same decrease as in table 6, when 2.0 m.e. K and 0.8 m.e. Na (44 per cent of the total amount of 6.4 m.e. cations) were added with  $\text{NH}_4$  as the form of nitrogen. With nitrate, apart from the

TABLE 9

*Dry weights and cation contents of plants receiving  $\text{NH}_4$  and nitrate nitrogen on acid-extracted soil with additions of 6.4 m.e. cations in varying ratios (second experimental year)*

EXCHANGEABLE CATIONS PER 100 GM. SOIL				YIELD OF DRY MATTER PER POT		CATION CONTENT OF PLANTS*							
Ca	Mg	K	Na	$\text{NH}_4\text{-N}$	$\text{NO}_3\text{-N}$	Ca		Mg		K		Na	
m.e.	m.e.	m.e.	m.e.	gm.	gm.	$\text{NH}_4\text{-N}$	$\text{NO}_3\text{-N}$	$\text{NH}_4\text{-N}$	$\text{NO}_3\text{-N}$	$\text{NH}_4\text{-N}$	$\text{NO}_3\text{-N}$	$\text{NH}_4\text{-N}$	$\text{NO}_3\text{-N}$
						m.e.	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.
5.45	0.6	0.25	0.1	23.7	27.5	22.5	20.5	22.5	25	41	35.5	21.5	17
5.1	0.6	0.5	0.2	27.0	32.1	16.5	16	17	20	61	52	20	18
4.5	1.2	0.5	0.2	25.8	34.7	14.5	12	20	19	67	49	21	15.5
4.4	0.6	1.0	0.4	27.9	37.1	13.5	13	12.5	13.5	97.5	79.5	9.5	10.5
3.8	1.2	1.0	0.4	27.6	34.4	11	9	16	14.5	101.5	82	10	9.5
2.4	1.2	2.0	0.8	16.3	36.0	5	6	11.5	13	109	90	10.5	13

\* Per 100 gm. dry matter.

higher level of all these groups, this last group especially showed no unfavorable influence of the chosen cation ratio; the plants exhibited no abnormal symptoms as did those in the corresponding  $\text{NH}_4$  group, which were dwarfed and yellow-striped, probably as a result of Ca deficiency.

The cation contents of these  $\text{NH}_4$  and nitrate series are also given in table 9. The principal difference is the markedly higher K content of the  $\text{NH}_4$  series; in general, Ca is also slightly higher in the  $\text{NH}_4$  series; for Mg and Na, the differences are irregular. It is undeniable that with the somewhat higher Ca and Mg contents and the lower sum of K and Na, the composition of the nitrate-treated plants of the last group seems somewhat more favorable for normal growth than that of the  $\text{NH}_4$ -treated plants. In our opinion, however, the great difference in production cannot be explained solely by this small difference in cation composition, and we are inclined, therefore, to assume as a hypothesis that the  $\text{NH}_4$ -treated plants in this case needed more Ca for normal growth than did the nitrate-treated ones.

From the few examples cited here, the importance of the form of nitrogen in the study of cation equilibria in the plant is evident; the cation ratio in the plant, as



related to that of the culture medium, does not seem to be fundamentally different, however, whether  $\text{NH}_4$  or nitrate is used. The problem resembles that of the influence of the form of nitrogen on K deficiency, encountered by many authors, and is beyond the scope of this paper.

#### *Relations of individual cations*

*Potassium.* The relation between the uptake by the plant and the exchangeable ion present in the soil is simpler for K than for the other three cations. In plants grown on normal soils with an adequate K supply, the content of K dominates that of the other cations. In our first publication on this subject<sup>9</sup> we correlated the cation uptake by the plants with the following relationship of the exchangeable cations of the soil:

$$\frac{20\text{K}}{0.1 \text{ Ca} + 0.2 \text{ Mg} + \text{Na}}$$

This indicated the slight influence of Ca, the somewhat increased influence of Mg, and the greatest importance of the Na in relation to K uptake. In the experiments of the present paper, however, the ratio of K to Na remained constant, and, therefore, such a formula could not be tested. The discussion of the data of table 8, however, indicated a small decrease in K content when a greater part of the Ca was replaced by Mg and suggested, also, a possible depressing effect of the highest Na content on the K uptake. These are, perhaps, examples of the increasing influence on the K content when Ca is partly replaced by Mg or Na.

A complication in this relationship, demonstrated in table 7, was the apparent difficulty of uptake or the small availability of K with low pH values of the soil. We have seen that as pH values rose from about 4 to 5, as a result of increasing additions of  $\text{CaCO}_3$ , the K content of the plant increased, and only on further additions, resulting in further rise in pH, did the ordinary mutual replacement of K by Ca in the plant occur. It is to this replacement only that the aforementioned formula refers.

To sandy soils, on which all our experiments on ion equilibria have been made and for which the given rules will apply, rarely will additions of  $\text{CaCO}_3$  be large enough to depress greatly the K uptake. Neither will such high concentrations of Na or Mg occur in ordinary soils that these ions will have much influence on the K uptake. We can assume, therefore, for the sake of simplicity, that the K uptake in the plant as a whole is directly proportional to the concentration of exchangeable K in the soil; only at low pH values will the uptake, as a rule, be less than would be expected from the concentration of exchangeable K.

In these experiments, the K content of 100 gm. of dry matter from the plants ranged from 20.5 m.e., when no K was added to the acid-extracted soil, to 162, when 2.25 m.e. K was added as the carbonate to 100 gm. soil, that is, 2,115 kgm.  $\text{K}_2\text{O}$  per hectare (2 million kgm. of arable soil). No such extremes will ever be reached in practice, but for the much smaller range usually covered, the simple relationship between soil and plant value for potassium will also hold true.

*Sodium.* The much more complicated relationship between soil and plant

<sup>9</sup> See footnote 2.

with regard to uptake of Na has already been mentioned. Although for all groups the K:Na ratio added was the same, namely, that in the original soil ( $2\frac{1}{2}$ :1), the ratio of K and Na taken up by the plants by no means remained the same. Figure 1 gives a complete survey of the course of both K and Na contents with increasing additions for seven different series. Most of the values are averages of groups receiving two different Mg additions.

In each series, the smallest addition of both ions, usually causing the greatest increase in K content, decreased the Na content or kept it at the initial level. Only when the K content failed to increase much further with the highest additions in some of these series did the Na uptake again increase. In general, it may be said that, when small concentrations of both ions are added, the uptake of sodium is wholly dependent on the uptake of K, but when further additions of both ions fail to increase the K uptake much more, Na can be taken up to a greater extent. The most striking example of the decreasing Na content

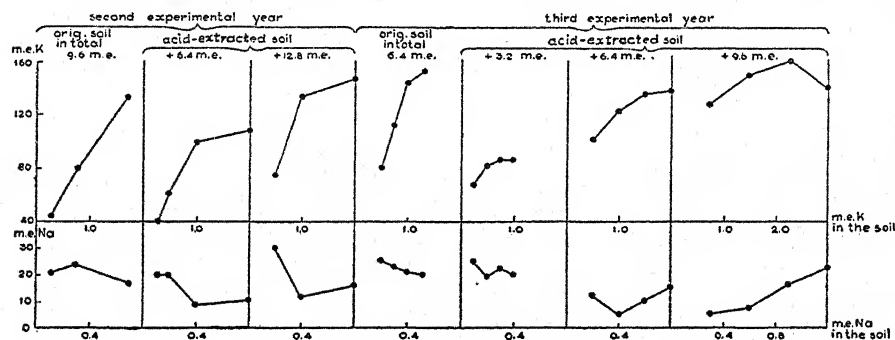


FIG. 1. PLANT CONTENTS OF K AND Na WITH INCREASING ADDITIONS TO THE SOIL OF K AND Na IN CONSTANT RATIO FOR SEVEN DIFFERENT SERIES

of the plant due to addition of Na and K together is the value already mentioned of 62 m.e. Na to only 20.5 K, when neither ion was added to the acid-extracted soil; with an addition of 0.5 m.e. K and 0.2 Na, the ratio became 21.5 Na to 75.5 K, whereas a large addition of 2.0 m.e. K and 0.8 Na lowered the Na content still further to 13 m.e. and increased the K to 115.5 m.e. in 100 gm. of plant material.

The constant ratio of Na to K in these experiments again makes it impossible to establish a quantitative relationship between the Na concentrations in soil and plant. The same conclusion, however, can be drawn, namely, that *the Na content of the plant is dependent primarily on the K uptake, or the K content of the soil; with varying K to Na ratios in the soil, it is this ratio that determines the uptake of Na*. The other cations Mg and Ca are of only secondary importance in the Na uptake. As has been pointed out<sup>10</sup>, the Na uptake of plants on normal soils is of importance to but few species. For some other species, including oats, used in these experiments, Na uptake becomes important only in the case

<sup>10</sup> Itallie, Th. B. van. The role of sodium in the cation-balance of different plants. *Trans. Third Internat. Cong. Soil Sci.* 1: 191-194. 1935.

of K deficiency. In other cases, even when considerable amounts of Na are present in the soil or are added to it, the uptake by these plants remains low, being dominated by K taken up in excess.

*Calcium.* The scheme of these experiments makes it possible to study only the effect of increasing additions of Ca or Mg or of Na + K together with de-

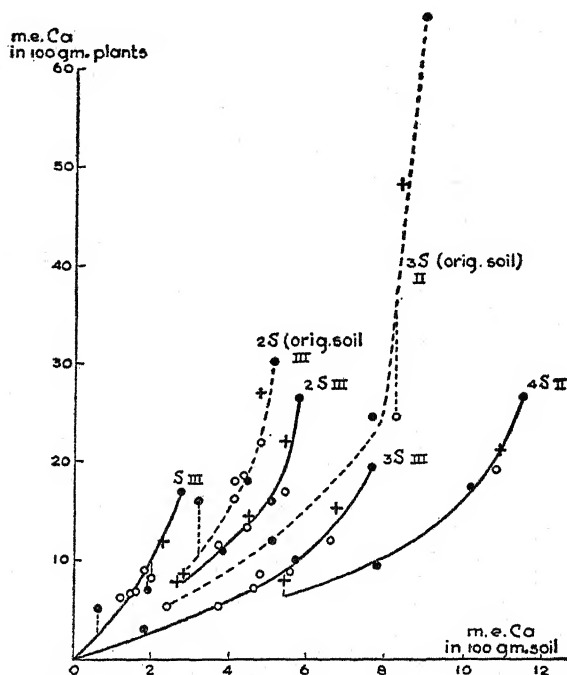


FIG. 2. Ca CONTENTS OF PLANTS OF VARIOUS SERIES IN RELATION TO EXCHANGEABLE Ca CONTENTS OF THE SOIL

+ Ratio  $\frac{\text{Mg}}{\text{K} + \text{Na}}$  greater than that in original soil.

● Ratio  $\frac{\text{Mg}}{\text{K} + \text{Na}}$  equal to that in original soil.

○ Ratio  $\frac{\text{Mg}}{\text{K} + \text{Na}}$  less than that in original soil.

creasing additions of one, two, or all the other cations. When the Ca contents of the plant are plotted against the exchangeable content of this ion in the soil for six experimental series (fig. 2), the values for each series fit a different curve fairly well.

To indicate the ratio of the other ions, Mg on one hand, and K + Na on the other, the values are marked in three different ways in the diagram, according to this ratio. In most cases, for corresponding Ca contents in the soil, the Ca contents of the plants in each series are a little higher when the ratio Mg to

alkali ions is greater than that in the original soil than when the ratios are equal to or smaller than that in the original soil. From left to right in the diagram the curves have a gentler slope, the greater the total amount of cations. The curves for the original soil series lie distinctly more to the left than those for the series with equal cation additions to the acid-extracted soil. The result of these differences in the course of the curves is that for one Ca value in the soil very divergent Ca contents in the plants are recorded; for example, for 5.1 m.e. in the soil, the plant contains from 30 to 6 m.e. This same amount of 5.1 m.e. Ca in the soil, however, represents in each series a very different proportion of the sum of the cations; that is, 80 per cent in series 2 S, 53 per cent in series 3 S, and 40 per cent in series 4 S. Furthermore, we have already advanced the hypothesis that in the acid-extracted soil not all of the added Ca is present in the exchangeable form, which is readily available to the plant, and that therefore these percentages in reality are lower for the acid-extracted series. This fact should account, then, for their lower position in this diagram in comparison with the curves of the original soil series. It is clear that when the Ca contents of the plant are plotted against the percentages of calcium in the sum of cations in the soil instead of against the quantity of Ca, a more satisfactory relation, holding true at least for all series with the acid-extracted soil, can be expected. This is shown in figure 3, in which allowance is made for varying ratios of Mg and K + Na. Instead of taking for the abscissa the ratio  $100 \text{ Ca} : [\text{Ca} + \text{Mg} + 2(\text{K} + \text{Na})]$ , thus indicating the greater depressing action of the alkali ions than of Mg on the Ca uptake.

Figure 3 shows that all dots for the four acid-extracted series of figure 2 fit one curve fairly well, whereas those of the two series with the original soil fit another one. If we were to take smaller values for the exchangeable Ca content of the acid-extracted and base-treated groups, it would be possible to make the curve for acid-extracted soil coincide with that for the original soil.

The conclusion to be drawn from figure 3 is that the Ca content of the plants depends largely upon the percentage Ca of the sum of the four cations added to the soil by replacement of the H ions. The absolute amount of cations and especially of Ca itself, and the related pH value of the soil, have only a relatively small influence on the Ca uptake of the plants. It makes some difference, however, whether the greater part of the other cations is added as Mg or as alkali ions, the latter depressing the Ca uptake more than does the Mg.

*Magnesium.* The Mg ion assumes an intermediate position between Ca and the alkali ions. In ordinary soils, the quantity of exchangeable Mg is much less than that of Ca, but the former is much more readily taken up by plants. We have seen, for example, that from equivalent quantities of both ions in the exchangeable form about three times as much Mg is taken up. Generally, the exchangeable Mg content of the soil is greater than that of Na and K, but these ions are again taken up more readily than Mg.

The scheme of these experiments makes it possible to study the Mg uptake under varying conditions of cation ratios. With constant alkali additions, increasing Mg, and decreasing Ca, the Mg content shows a regular increase.

On the other hand, with constant Mg and increasing alkali additions, the Mg content is markedly lowered, indicating the importance of K and Na for the uptake of Mg.

The upper half of figure 4 shows the course of the Mg uptake in the plant with the exchangeable Mg values of the soil as the abscissa for the series in which 6.4 m.e. cations was added to the acid-extracted soil in the second and third experimental years and for the original soil series to which 3.2 m.e. was

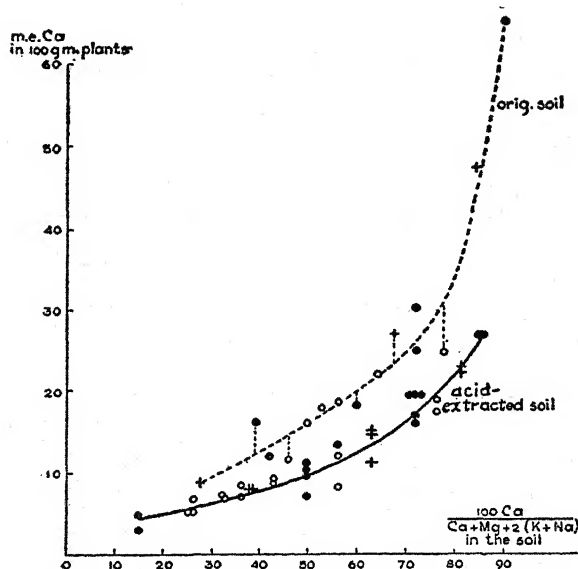


FIG. 3. Ca CONTENTS OF PLANTS OF VARIOUS SERIES IN RELATION TO RELATIVE Ca CONTENT OF THE SOIL

- + Ratio  $\frac{\text{Mg}}{\text{K} + \text{Na}}$  greater than that in original soil.
- Ratio  $\frac{\text{Mg}}{\text{K} + \text{Na}}$  equal to that in original soil.
- Ratio  $\frac{\text{Mg}}{\text{K} + \text{Na}}$  less than that in original soil.

added (making the total content 6.4 m.e.). For each alkali level we can connect the Mg values; the higher the alkali additions, the lower the Mg curves. When, however, we plot the Mg content of the plant, not against the Mg value of the soil but against the ratio of  $\text{Mg}:(\text{K} + \text{Na})$ , the relation becomes much more homogeneous (lower half of figure 4). For the original soil with 6.4 m.e., the same holds true, but the curve has a different slope. For the same Mg values of the original soil, we find more Mg in the plant, thus indicating, just as for Ca, that in the acid-extracted soil not all of the added Mg is in the exchangeable state and thus available. The influence of the alkali ions on the uptake is, however, the same.



Similar diagrams can be made for the Mg values of the series with 3.2, 9.6, and 12.8 m.e. cations, but they cannot all be made to coincide with the one

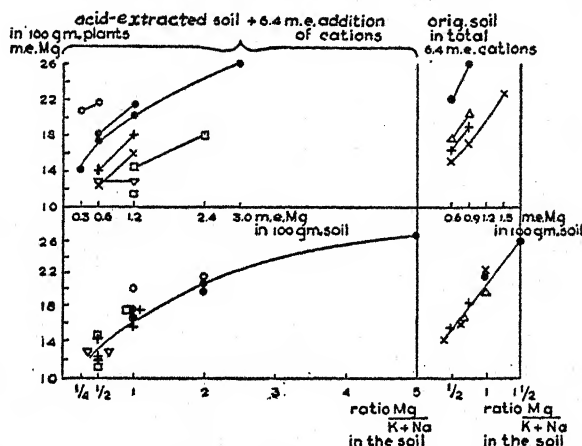


FIG. 4. Mg CONTENT OF PLANTS IN RELATION TO Mg CONTENT OF THE SOIL (UPPER HALF) AND TO Mg: (K + Na) RATIO IN THE SOIL (LOWER HALF)

- = 0.25 m.e. K
- = 0.5 m.e. K
- △ = 0.75 m.e. K
- + = 1.0 m.e. K
- × = 1.25 m.e. K
- ▽ = 1.5 m.e. K
- = 2.0 m.e. K

On lower abscissa 1 = ratio original value,  $\frac{0.3\text{Mg}}{0.25\text{K} + 0.1\text{Na}}$

TABLE 10

Mg contents of plants grown with constant Mg and alkali and varying Ca additions to the acid-extracted soil (N as  $\text{NH}_4$ )

CATIONS ADDED TO THE SOIL		MG CONTENT OF PLANTS*			
		THIRD EXPERIMENTAL YEAR		SECOND EXPERIMENTAL YEAR	
		Total cations added		Total cations added	
Mg	K + Na	3.2 m.e.	6.4 m.e.	6.4 m.e.	12.8 m.e.
m.e.	m.e.	m.e.	m.e.	m.e.	m.e.
0.3	0.35	10	21.5	—	—
0.6	0.7	14.5	18	17	20.5
0.6	1.4	14	14.5	12.5	13.5
1.2	0.7	—	—	20	21
1.2	1.4	17	18	16	17.5

\* Per 100 gm. dry matter.

given here, because the Mg contents of the plants with small additions of 0.3 and 0.6 m.e. Mg are higher when more Ca is added to the soil. This symptom is often recorded on this type of soil. Table 10 gives some examples with 1 S

and 2 *S* cation additions and the same Mg and alkali additions in the third year and with 2 *S* and 4 *S* additions in the second year. Only in the first two lines of the table are the differences of importance.

As has already been mentioned, the ratio of Mg to the alkali ions in the original soil was too small for normal plant growth. On the original, as well as on the acid-extracted and cation-substituted soil, we found symptoms of Mg deficiency when the Mg contents of the plants were less than 15 m.e. per 100 gm. of dry matter. These contents were found with Mg additions of 0.3 m.e. as well as of 1.2 m.e. Mg to the soil, depending on the quantity of K and Na added and the pH value of the soil. Extensive research<sup>11</sup> has confirmed that Mg-deficiency symptoms will occur also on soils that contain a sufficient Mg supply when so little K is added that the Mg uptake is depressed beyond a certain point.

#### CONCLUSION

As a whole, in these experiments the cation uptake has been found to follow the same pattern in the acid-extracted soil as in the original soil. From this it may be concluded that the exchangeable cations present in a soil and those added by fertilizing, to replace H ions of the adsorption complex, have the same function in plant growth. The cations added to the acid-extracted soil can be regarded as of much the same importance as those present in the original soil. The probability that part of the Ca and Mg added to the acid-extracted soil does not remain in the exchangeable form and therefore is not available to the plants, does not interfere with this conclusion; more of these cations, however, have to be added to the acid-extracted soil to produce plants with the same contents as those grown on the original soil.

These experiments also demonstrated the feasibility of setting up all sorts of ion ratios in the soil, especially with small cation additions (low pH values) so that various ratios can be tried on different pH levels, when (as was the case in these experiments) all cations are added in the form of carbonates. Naturally, the mutual cation ratios might be extended far beyond those chosen here, in which chiefly the relation Mg to K + Na is varied; then more extensive relationships between the soil and plant values could possibly be drawn up. Much more definitely than heretofore, the fundamental conclusion drawn from these experiments is that for Ca, Mg, and Na the absolute amount present in the exchangeable form is not primarily the determining factor for the uptake of these ions by the plant, but rather its ratio to one, two, or all three of the other cations. Of most importance are all three other ions for Ca, especially K and Na for Mg, chiefly K for Na. In these experiments with constant K:Na ratio, the potassium uptake, on the other hand, is dependent only on the K concentration in the soil; it makes but little difference whether Ca or Mg forms the greater part of the cations present.

The results, as a whole, even in the very extreme cases included here, agree with those of earlier experiments on normal soils; they may, therefore, be applied to ordinary field conditions on sandy soils.

<sup>11</sup> Itallie, Th. B. van. Magnesiummangel und Ionenverhältnisse in Getreidepflanzen. *Bodenk. u. Pflanzenernähr.* 5: 303-347. 1937.

## SUMMARY

Culture experiments carried out during three successive years with a soil first treated with dilute acid to remove the exchangeable bases and then supplied with cations in the form of carbonates are described. As a comparison, tests with the soil in its original condition were included. This treatment of the soil makes it possible to study plant growth and ion uptake from the following standpoints:

In relation to only one group of cations, namely, those added after the treatment, instead of to the usual two kinds, those already present in the exchangeable state and those added with the fertilizers.

With all sorts of ratios between the added cations Ca, Mg, Na, and K at different cation levels (varying pH values).

The cation additions to the acid-extracted soil were made on the basis of the analysis of exchangeable ions in the original soil, so that the total quantities added amounted to one, two, three, or four times the original value. In each series, with the same total quantity added, the ratio of the four cations varied greatly. Extra quantities of carbonates were also added to the original soil in the same ratios. In some series the basic  $\text{NH}_4$  fertilization was changed to nitrate.

As was to be expected with the sandy soil used, which was deficient in Mg and had a pH value of 4.2, every addition of carbonates to the original soil (or addition to the acid-extracted soil of more cations as carbonates than the original amount so that the pH value was raised), caused better plant growth. The Mg-deficiency symptoms found in cereal crops on the original soil appeared also in comparable groups of the untreated soil.

Plants grown on the cation-substituted soil were more affected by the varying influences on plant growth, and showed greater variations in yield in the different years, than those grown on the original nontreated soil.

On the basis of soil analyses before and after the acid treatment, the suggestion is made that the acid not only removed almost all bases present in the exchangeable state but also a small part of the Ca and Mg present in other forms. Of the added carbonates, a small part will likely be used to supply this loss of non-exchangeable cations so that a little less than the original cation value will now exchange with the H ions of the adsorption complex. In agreement with this suggestion, the pH value in the cation-substituted soil is, for the most part, somewhat lower than that of comparable groups of the original soil, and the uptake of bases indicates, also, a lower availability of Ca and Mg to the plant.

Notwithstanding the differences in growth and yield on original and treated soil, the manner in which the cations were taken up was fundamentally the same. This leads to the conclusion that for plant growth the cations present in the exchangeable state have the same function and the same importance as those added to the soil as carbonates in this experiment.

Plant growth became seriously affected when more than about a fourth of the Ca present in the ratio of the original soil was replaced by K and Na, with

nitrogen added in the  $\text{NH}_4$  form. Such a replacement of Ca by Mg did not, however, cause a deterioration in plant growth.

Nitrogen added as nitrate improved plant growth especially in comparison with  $\text{NH}_4$ , which was not readily utilized at low pH values or under conditions of unfavorable cation ratios.

The following general survey of the uptake of the four cations is outlined in a series of diagrams:

The Ca uptake is wholly dependent on the ratio of Ca to the other three cations in the soil and not on the absolute quantity added. The part of K and Na in this ratio is slightly more important than that of Mg. Ca-deficiency symptoms are narrowly correlated with low Ca contents in the plants; such symptoms occur also with large additions of Ca at high pH when alkali ions in large quantities also are added.

The ratio of Mg to the alkali ions in the soil chiefly determines the Mg content of the plant. As with Ca, it is possible, therefore, for plants to be low in Mg and exhibit deficiency symptoms when the supply of Mg is sufficient if, at the same time, the alkali additions are large. Increasing Ca supplies slightly favor the Mg uptake, especially with small additions of Mg.

The uptake of Na and K in these experiments was studied at only one ratio, namely, that of the original soil (0.25 m.e. K:0.1 m.e. Na).

The Na uptake depends chiefly on the uptake of K. When with increasing additions of K and Na in the constant ratio, the K content of the plant rises, the Na content usually decreases. Only with fairly large alkali additions, when the K uptake fails to increase much more, does the Na content begin to increase markedly. Mg and Ca additions have no appreciable influence on the Na uptake.

The K uptake in these experiments is, as a whole, affected only by the K additions to the soil. Only at low pH values of the soil is the K uptake favored by addition of Ca as the carbonate; otherwise, this ion does not interfere with the K uptake.<sup>12</sup> Replacement of most of the Ca by Mg depresses the K content of the plant. The influence of Na on K was not studied here.

In general, the results agree well with those of previous experiments on cation uptake. The special scheme including the extreme ratios made possible, however, a better insight into the uptake of Ca and Mg at different cation levels.

<sup>12</sup> See footnote 7.

## NOTES ON THE INTERNATIONAL CONFERENCE OF PEDOLOGY IN THE MEDITERRANEAN REGION<sup>1</sup>

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### CONFERENCE BACKGROUND

It was a bold stroke of the French section of the International Society of Soil Science to call a pedologic conference in May 1947, while echoes of the guns of World War II were still reverberating from many troubled areas and when Europe itself was struggling through a period of complex economic, political, and social unrest. To convene an international meeting under these trying circumstances called for courage and a spirit of adventure. In a way, this adventure was befitting the traditional revolutionary spirit of France, and the French section of ISSS is to be congratulated on its initiative in getting the international wheels of organized soil science rolling again.

When the call for the conference was sent out, there was skepticism over the possible success of the undertaking. For a long time no definite date was set for the conference, and after one had been agreed on, it was at the last minute moved back 12 days. This change prevented many delegates from attending. In fact, many American delegates who had planned to participate were forced to abandon the idea.

As the conference got under way, it was clear that our French colleagues were eager to start the International Society of Soil Science on its program from the point where it left off at the Third International Congress held in 1935 at Oxford, England. It is to be recalled that that congress was supposed to have conducted an excursion through the Mediterranean to study the red soils, the so-called terra rossa. For those who attended both international gatherings of the soil scientists, the 1947 conference was just a continuation of the unfinished work of the third congress.

### CONFERENCE CONSTITUENCY

All through the three weeks of the conference, the prevailing atmosphere was pedologic. Profile studies and discussions kept in the background topics not related to pedology. Still, the subject matter of some papers was far from pedologic. A report on an elementary study of ion intake by plants in solution culture, an elementary discussion on plowing, and a popular paper on erosion could hardly be defended as appropriate topics for a pedologic conference. Nor was the constituency of the conference pedologically strong enough to wrestle with the vociferous geologists, botanists, foresters, pomologists, agronomists ("crops men," in American parlance), and agriculturists in general who

<sup>1</sup> Paper of the Journal Series, New Jersey Agricultural Experiment Station, Rutgers University, department of soils.



were interested in pedology either not at all or only indirectly. The writer is not so extreme a purist as to wish to exclude from a pedologic conference any one who is not a pedologist, and the presence at this conference of the alert and spirited group of geologists was especially welcome. Their bellicose attitude toward the pedologists' viewpoint exhibited not so much the strength of the geologists as the weakness of the pedologists.

A reason for the complex composition of the pedology conference is, perhaps, the confusion still existing among agriculturists as to the meaning of the term *pedology*. This term is frequently used synonymously with the broader term *soil science*, or as our British, French, and Russian colleagues would perhaps like to call it—the *science of the soil*. As a matter of fact, though we know that pedology is only one branch of soil science, the preface to the program of the conference<sup>2</sup> includes the following statement: "La Pedologie, ou science du sol, est une discipline jeune (Pedology, or the science of the soil, is a young science)." Not surprising, therefore, was the large attendance of nonpedologists with the few pedologists. Many delegates with very little appreciation of pedology presented papers far removed from pedology. This anomaly will be reflected in the published proceedings of the conference and need not be elaborated on here.

Much to be regretted was the failure of the Russian delegates to come to the conference. Any one familiar with the stock in trade of Prasolov and Polynov, the two leading men of the group that were to have comprised the Russian delegation, had grounds for disappointment over their absence. The conference lacked the authoritative opinion of these men on questions of soil genesis, nomenclature, and fundamental principles of pedology. On the other hand, the Russian colleagues missed a singular opportunity to study at first hand the Mediterranean red earths, a type of soil not encountered in the USSR.

The number of foreign countries represented at the conference hardly justified the high-sounding name "International Pedologic Conference." In all, 9 countries sent 22 delegates. Of these, Great Britain supplied 8; Belgium, 4; United States, 3; Switzerland, 2; and Holland, Norway, Sweden, Palestine, and Portugal, 1 each. Besides, there were representatives from Morocco (the most distinguished among them, the veteran del Villar, a refugee from Spain), Tunisia, and Algeria. Of course, France was out in full force, with a large proportion of the younger generation engaged in soil work.

One should not, however, underestimate the importance of the conference because of the poor attendance. From an educational standpoint, the conference brought to the fore two points: First, for the present, at least, there is not much enthusiasm among the pedologic forces in western Europe. Undoubtedly, the havoc of war has contributed much to the general apathy. Second, concentration on a particular sector of the broad front of pedology can be most fruitful.

A redeeming feature of the conference was the excursions and field trips, during

<sup>2</sup> For some reason, the original official program issued by the French section of the ISSS for the sessions in Montpellier speaks of "*Congrès International, de Pedologie*," instead of "*Conférence Internationale de Pedologie Méditerranéenne*."

which the pedologic atmosphere prevailed. These trips began as the sessions opened in Montpellier, continued as the delegation moved through southern France to Marseilles, and formed an important part of the program throughout the 10 days in Algiers. From printed descriptions of the characteristics of profiles examined in the itinerary, it is clear that the aim was to afford an opportunity for study and exchange of opinion on the nature of the complex red soils in the Mediterranean region.

The itinerary was followed remarkably closely, with only minor breaks in the schedule and in the order of the day and with meticulous care and thoughtfulness for the comfort of the delegates. The organizing committee and the French delegates of the conference deserve the thanks, not only of the participants of the conference who benefited directly, but also of all interested in the science of soils who will benefit through contact with the delegates and from the forthcoming proceedings. These sentiments were expressed on many occasions by the spokesmen of the various delegations during the conference sessions and the excursions.

#### EXCURSION RECORD

A critical review of the descriptive material on the soil profiles examined during the excursion shows that in some cases the deductions made were not in line with the data. The data also indicate that not enough care was exercised in selecting the profile sites. There seemed to be a tendency to stress a single characteristic, such as color, with no consideration for the profile constitution. A few examples may illustrate this point.

A supposedly yellow soil, described on page 69 of the May 8 program,<sup>3</sup> was found to be nothing more than an immature soil on lime marl. Except for the yellowish brown layer at the 5-25-cm. depth, no morphological or chemical property indicated association of this soil with the yellow soils.

The *terra rossa* profile, listed on page 71 of the program, appeared to be a poorly drained soil on transported material, the profile of which was obscured by difference in texture at various depths. The 5-25-cm. layer was brown to gray-black and was permeated with mycelium of mushroom fungi. The hydrogenic origin of this soil was evidenced by the organic matter content of the so-called profile. Starting with 6.99 per cent at a depth of 3 to 10 cm., the organic matter decreased to 1 to 4 per cent at the 30-150-cm. depth, and was still 1.22 per cent at the 2-m. depth. The entire depth was alkaline, pH 7.4-8.3, indicating, perhaps, an early salinization-desalinization effect.

A description of a podzolized profile on a silicious schist is given on page 83, of the program. Whereas the nature and properties of this profile definitely place it in the zone of podzolization, its distinguishing specific constitutional characteristics were found to be of more significance than its zonality type. The data on organic matter show that the A<sub>1</sub> horizon (20-25 cm. deep) has 4.68 per cent; the A<sub>2</sub> horizon (30 cm.), 3.28 per cent; the B horizon (25-30 cm.),

<sup>3</sup> Congrès International de Pedologie de Montpellier—Alger, Mai, 1947. Programme et Renseignements ayant traités au Congrès de Montpellier, Jeudi, 8 Mai.

3.31 per cent; and the C horizon, 2.89 per cent. Such a distribution of organic matter in a podzol profile places it not in the typical eluviation series of soil formation, but in the hydromorphic series. The absence of alkaline earth bases with an excess of silica is a clear-cut indication of the probable effect of the lithogenic character of the parent material. In short, the soil is not just a podzolized soil, but is, rather, a hydromorphic-lithogenic member in the zone of podzolization.

*Excursion in southern France*

En route from Montpellier to Nimes, the color of the prevailing soil landscape as it appeared through the window of a speeding autobus was brown to red, reminding one that this must be the beginning of the much-described but little-known *terra rossa*. Miles and miles of vineyards, with bushy grapevines of mixed gray-green on the lower sides of the leaves and of dark green on the upper sides, offered a sharp color contrast to the soil in the middles, kept clean of weeds by some special cultivator which gave the ground a rough clumpy surface. Here no one could doubt the dark brick-red color of the soil.

No stops were made until the valley in the region of Lunel was reached. The color of the soil on the flat topography of the valley rising gradually toward the hills on the horizon changes from gray-brown at the lower drainage level to brown and red-brown at the higher drainage level. The profile examined consisted of a sandy surface layer merging into clayey loam resting on a calcareous deposit or on loamy calcareous material. There was no horizon differentiation in the exposed profile. It was obvious that at the lowest drainage level the saturation of the material had prevented oxidation, causing a retardation of weathering and giving rise to the formation of claylike materials. At the higher levels, laterization was going on unimpeded, and the separation of the oxides of iron gave the color.

Leaving Lunel, the excursion proceeded over loess or loess-like soils, free of lime, according to the nomenclature given by the geologists who worked in the region. This material did not look at all like the loess of the Missouri watershed or of the chernozem region of the European Russian plain.

At one point a profile that showed distinct efflorescence of limestone of the pseudomycelium type was examined. The color of the soil, in spite of the presence of calcium carbonate, was not red. Discussion of the anomaly with the local men brought out the fact that the limestone is the result of upward movement of salts. This means waterlogged conditions, under which the processes of eluviation and laterization are impeded.

On the way from Nimes to Marseilles, the soils formed on the prevailing types of limestone parent material, from hard dense limestone through soft and marl limestone. The route led through the valley of the Rhone River over fields of alfalfa and grain. In the region of the old delta, saline soils were examined. The profile revealed indications of solonetzic character, probably of an earlier period. At present, the high water table is causing a secondary salinization, and the soil is thus a secondary solonchak.

On the limestone ledges of the ruins of a flour mill of Roman days at Bardegal, black to dark brown soil material not exceeding 2 or 3 cm. in thickness could be found in the depressions. It was named *rendzina*. It did have the granular structure of *rendzina*, but this little mass of black soil in depressions on the slope could be interpreted as a local limited occurrence. There were just as many red spots as black.

#### *Excursion through Algeria*

Upon arrival at Algeria, the pedology conference settled down for a few days in the city of Algiers for more professional papers, chiefly on the soils of North Africa. With the exception of a few papers of minor importance, most of the papers were illustrated with excellent charts and maps, covering the geology, climate, vegetation, agriculture, and soils of the respective areas. It is to be hoped that these maps and charts will be incorporated in the published proceedings to supplement the analytical and descriptive data. Many of the papers on pedology were devoted to the role of parent material in the formation of terra rossa, especially with reference to its color, as a relict of an earlier humid tropical climate. This opinion, suggested by the author in an other connection<sup>4</sup>, was expressed by del Villar. It is very likely that modern physicochemical and mineralogical studies of soils will disclose the specific properties of the two types of red soils, the terra rossa and the red loams, to be the result of superimposition of the reactions of the present climate on relicts of laterite of an earlier humid tropical climate.

The excursion through Algeria brought out very clearly the fact that whereas terra rossa was quite evident in southern France, the genuine type is to be found in Algeria where the distinctive Mediterranean climate (winter concentration of precipitation and dry summers) has been responsible for the characteristics of the soils. No one travelling through Algeria can doubt that red soils predominate, and terra rossa must, therefore, represent a specific type of soil formation.

In the Mitidja plain on the Algiers-Boufarik-Blida route the soils are dark brown to black, with oases of reddish brown to brown on the more elevated spots of the plain. Similar soils were observed in the valleys along the railroad line from Algiers to Relizane and in the many other valleys visited during the excursion. Examination of these soils, mostly heavy loams, clay loams, and occasionally those of lighter texture (and these are usually not so dark as the heavier soils), disclosed their relationship to the tirs of Morocco or the regur of India. The origin of these soils has been expounded by del Villar<sup>5</sup> in his researches on the tirs of Morocco. These soils have formed under conditions of poor drainage. The process of soil formation and the reactions involved, as advanced by prominent students of laterization, are associated with reduction of iron during the period of poor drainage, loss of iron into the ground waters, and an accumulation

<sup>4</sup> JOFFE, J. S. Climatic sequences of the Post-Wisconsin glacial age is revealed in the soil profile. *Soil Sci. Soc. Amer. Proc.* (1941) 6: 368-372. 1942.

<sup>5</sup> DEL VILLAR, E. H. The tirs of Morocco. *Soil Sci.* 57: 313-339. 1944.



of alumina and hydrous aluminum silicate, usually of the montmorillonitic type of clay minerals. At the time of continuous waterlogging, organic matter accumulated. This was subjected to vigorous chemical and biological oxidation during intermittent droughts and to even more vigorous oxidation after the permanent drop of the water table. Only the difficultly oxidizable humins and probably some bitumens remained behind, and it does not take much of these substances to color the matrix dark brown to black. Soils with a similar dark color in the temperate zone would contain 6 to more than 8 per cent organic matter, whereas in the tropics these soils carry, as a rule, not more than 1 to 1.5 and only rarely more than 4 per cent organic matter.

On a trip from Blida up the Atlas Mountains, we had an opportunity to get a close view of the ravages of erosion inaugurated by deforestation and grazing by goats of the Arab nomads. The denuded mountain slopes weather rather rapidly and supply vast masses of debris which are carried during the rainy season to the stream channels of the el-Kebir River and its tributaries. The ancient city of Blida and the adjacent settlements are threatened by the ever-increasing devastating floods. The French forestry and soil conservation services are making frantic efforts to save the city and the adjacent plain from being swept away and buried under the debris. Complex systems of terracing and reforestation dot the surrounding mountain slopes, starting from an altitude of about 5,000 feet down to the valley lying at about 1,000 feet above sea level. In many places the gullies are planted to cacti, which seem to take over the land and stop erosion. It is of interest that the multitude of terraces, 50 to 60 feet apart, are planted to fruit trees—figs, almonds, olives, and carob.

The soil on the slopes is grayish brown, coarse in texture, reflecting its lithogenic characteristics schistose origin. At an altitude of 2,500 to 3,000 feet, in a depression on a flat area, the author found accumulated dark colored A<sub>1</sub> material extending to a depth of about 3 feet, underlain with finer textured material, in all probability of the original B horizon.

The zigzag route of the excursion through Algeria (around the geographic points of Algiers, Relizane, Perregaux, Oran, Nemour, sidi-bed Abbes, Tlemcen, Oujda, El Aricha, and ending at Oran), in areas with 40 inches of rainfall in the north and 8 inches in the south, presented the delegates of the conference with an opportunity to examine a great many profiles. Most of these, like those examined in France, were selected apparently not so much for the clarity of their pedologic features as for the well-worked-out geomorphologic and geologic characteristics which were ably and clearly presented by the French geologists of the party. The weak position of the pedologists who selected the profiles can perhaps be explained by the difficulties involved in delineating pedologically any soil complex of the orogenic-lithogenic series, the kind that predominates in Algeria.

In the vicinity of Nedromah, not far from the historical Colonne de Montagnac<sup>6</sup> a dark to black profile exposed in a road cut was examined. Aubert, one of the best informed young French workers, with strong pedologic leanings still not

<sup>6</sup> Conférence Internationale de Pedologie Méditerranéenne, 1947. Excursions en Algérie, p. 71. Assoc. Français pour l'Étude du Sol, Paris.



fully crystallized, designated this soil as rendzina. Indeed, the layer of black soil, more than 3 feet deep, underlain by grayish white clay did have the morphological semblance of rendzina. According to data supplied by Aubert, the 0-70-cm. layer contains 16 per cent  $\text{CaCO}_3$ , followed by a layer containing 11 per cent, increasing to 20 per cent and going as high as 35-50 per cent, with underlying material containing only 8 per cent  $\text{CaCO}_3$ . It is clear that the parent material is not limestone. Besides, lack of horizon differentiation (there was some indication of heavier texture at the 2-foot level) and variation in texture indicated a colluvial origin. The topographic features of the area testified to this, inasmuch as they represented a kind of a natural terrace, at the point where the profile was exposed, on a long slope extending into the deforested and eroded hilly landscape. It is very possible that the accumulation of limestone was of vadose origin. If this could be established, and cursory examination of the geomorphologic features suggested it to be the case, then one could explain the low organic matter content of the soil. The 0-70-cm. layer had no more than 2 per cent organic matter, decreasing to 1.4 and 1.2 per cent at the lower level.

It appeared to the author that the two factors nonlimestone origin of parent material and low organic matter content of the so-called rendzina under consideration, coupled with the specific microtopographic position of the area, placed this soil in the tirs group. It is of interest to note that aside from the small area of so-called rendzina there were no black soils so far as one could see, despite seemingly identical parent material, topography, and climate. The soils in the neighborhood varied in color from brown to red. The natural terrace appeared to serve as an outlet for seepage waters, causing a waterlogged condition over a considerable part of the year. A closer study of the area and physical and chemical analysis of the black soil would be necessary to substantiate the deduction on the nonrendzina character of the soil. The structure of the black material and the dark colored streaks or tongue-like streamers over the grayish white to buff background below the 0-70-cm. layer certainly did not remind one of the rendzina on the chalk cliffs of Dover and Normandy or those in the vicinity of Oxford, England.

A somewhat different type of soil formation presented itself in the region of El-Aricha, one of the gateways to the great North African desert. Together with the mountainous landscape, the red soils disappeared from the horizon, and light chestnut-brown and brown soils made their appearance on an elevated plateau. Of the several profiles examined, depth was limited, and calcareous incrustated marls (Kunkar) and limestone rose close to the surface. According to del Villar, the lime accumulations are the result of upward movement of salts of an earlier geologic age when the water table was closer to the surface. Some elements of salinization observed in one of the profiles would substantiate the postulate of an upward movement. The great thickness of some lime crusts, however, is difficult to explain on this basis. There was not sufficient time to study the profiles in detail. Such study might have given clues to their genesis. There is this to be said: the brown and light chestnut-brown soils of these regions are related in color to the zonal chestnut and brown soils of the arid temperate

climate. The profile characteristics of the latter are in some measure molded by severe winter weather, which does not obtain in North Africa, although it does get fairly cold in winter. Still, the soils of the region of El-Aricha must be considered as a subtropical variety of arid type of soil formation. Chemical and mineralogical investigations on carefully selected typical profiles and the hydrologic history of the area would go a long way toward deciphering the genesis of these soils.

#### SUMMARY STATEMENT

Our French colleagues advanced their knowledge of the soils of the Mediterranean region in preparing the conference. They learned, in the course of the conference, that one of their weaknesses lies in not fully appreciating pedologic methods. Recognition of this shortcoming will serve as an incentive to return to the problem, dig up more typical profiles, subject the soils to a more critical pedologic analysis, and follow the more advanced chemical and mineralogical methods being used in soil studies in the United States and Russia.

## BOOKS

*Birds of Prey of Northeastern North America.* By LEON AUGUSTUS HAUSMAN. Rutgers University Press, New Brunswick, N. J., 1948. Pp. 164, figs. 32. Price \$3.75.

"The significance of the birds of prey to our entire economy is forcibly illustrated by the depredations of rodents to which we would be subjected were it not for the birds," writes the author in his introduction to this beautifully designed book. "The meadow mouse . . . and other subspecies merit a word by themselves in any discussion of the habits of our native birds of prey, since mice form such a large proportion of their dietaries, especially those of many of the owls. The meadow mouse . . . the most numerous mammal on the North American Continent . . . is one of the most destructive of all nature's forces with which those who produce our foodstuffs have to contend . . .

"In helping mightily in keeping down the numbers of those noxious forms our native birds of prey perform a very welcome service."

The author writes of three general classifications of birds of prey in northeastern North America—American vultures (order *Falconiformes*, family *Cathartidae*); American hawks, eagles, and their kin (families *Accipitridae* and *Falconidae*); and owls (order *Strigiformes*, families *Tytonidae* and *Strigidae*). Each of the 35 birds treated is described in some detail. The description covers appearance and size; notes and calls; habits of flight, breeding, nesting, and feeding; habitats; and means of identification.

The frontispiece pictures in color the red-tailed hawk (*Buteo borealis borealis*) in flight, and 31 full-page drawings by Jacob Bates Abbot show various species in their natural habitats and with their characteristic prey. A scientific classification of the birds, a selected nontechnical bibliography, and an index of vernacular names of birds of prey are appended.

*Chemical Composition of Plants as an Index of Their Nutritional Status.* By D. W. GOODALL AND F. G. GREGORY. Imperial Agricultural Bureau, Penglais, Aberystwyth, Wales, 1947. Pp. 167. Board covers. Price 9/(-).

This is Technical Communication 17 of the Imperial Bureau of Horticulture and Plantation Crops. It is an exhaustive review of methods of diagnosis of the mineral nutrient requirements of plants, diagnostic plant analysis, theoretical considerations involved, techniques employed in laboratory diagnosis, methods of reporting and interpreting results, factors that affect the accuracy of the diagnosis, comparisons of results of plant analysis with those obtained by plot tests, soil analysis, and field-observed deficiency symptoms. An excellent bibliography of some 900 papers is appended, as are also subject and author indexes. One of the most important features of the monograph is an extended table giving percentages of nutrients in plant material at the point at which deficiency symptoms become apparent and the names of the authors who reported them. In this table the material is classified by crops and elements.

Another of the 15 tables deals with the selection of organs for analysis; and a third, with the ratios of  $N-P_2O_5-K_2O$  that are suggested in the literature. The book is recommended to all those who are concerned with soil and plant diagnostic techniques.

*Colorimetric Methods of Analysis.* Third Edition. By FOSTER D. SNELL AND CORNELIA T. SNELL. D. Van Nostrand Company, Inc., New York, 1948. Pp. 239, figs. 109. Price \$4.50.

The first of a three-volume edition, this volume deals with principles, apparatus, and pH determinations. The other two volumes, now in preparation, will have to do with inorganic and with organic, biological, and miscellaneous determinations. Among the topics discussed in the several chapters are colorimetric methods, standards, photometry, nephelometry, turbidimetry, fluorometry, matters of accuracy, methods of calculation, and hydrogen-ion buffers, indicators, and methods of determination. The book is modern, well illustrated, and well documented and it contains a great variety of useful tables of data. It shows a picture of each instrument, diagrams its construction, tells how it is used, and provides a considerable amount of information concerning applications in its use. References are given to publications of some 500 workers in these fields. The book merits a prominent place in every modern laboratory.

*Forest Influences.* By JOSEPH KITTREDGE. McGraw-Hill Book Company, Inc., New York, 1948. Pp. 394, figs. 25. Price \$4.50.

The subtitle of this book is: "The Effects of Woody Vegetation on Climate, Water, and Soil, with Applications to the Conservation of Water and the Control of Floods and Erosion." The several chapters deal with climatic, soil, physiographic and forest regions, vegetation, light, temperature, wind, moisture, precipitation, interception, fog drip, evaporation, snow, soil relationships, transpiration, runoff, floods, erosion and its control, and watershed management. This book is of special interest in relation to the control of water. The chapter on vegetation for erosion control is an exceptionally good one in that it gives lists of trees, shrubs and vines, and grasses and herbs that can be used to best advantage for stabilization of banks and gullies, depending upon in which of the 17 natural-vegetation regions the area is located.

*Life, Its Nature and Origin.* By JEROME ALEXANDER. Reinhold Publishing Corporation, New York, 1948. Pp. 291, figs. 31. Price \$5.

This is a book on science in relation to living things, but it also contains a good bit of philosophy in relation thereto. It begins with a consideration of the origin of life, which is said to have had a very humble beginning, and then proceeds to a study of the smallest particles of matter, how molecules make masses, the importance of impurities, catalysis, catalysts, genetics, and evolution, ending with a chapter on philosophy, the guide to mental life. The book is rich in references to a great variety of observations made by other scientists that add much of interest and make it evident that the author has a wide ac-

quaintance with the whole field of science in relation to the subject under discussion. The chapter on impurities is of special interest to those dealing with plant and animal nutrition. Later in the book it is pointed out that "ashes of sponges" were used as a cure for goiter in the 13th century and that Boussingault suggested the addition of iodine to salt in 1833.

*Modern Colloids.* By ROBERT B. DEAN. D. Van Nostrand Company, Inc. New York, 1948. Pp. 303, figs. 97. Price \$3.75.

The subtitle of this book is "An Introduction to the Physical Chemistry of Large Molecules and Small Particles." The author's purpose is that of introducing the student to the subject of colloidal behavior. The material is presented in an especially lucid form, with excellent supporting illustrations. The several chapters deal with methods for determining size and shape of colloidal particles, liquid surfaces, adsorption, high polymers, plastics, resins and rubbers, carbohydrates and proteins, colloidal ions, emulsions and foams, hydrous oxides and silicates, and lyophobic colloids or suspensoids. A short list of selected references is presented at the end of each chapter, and more specific references are given at the bottoms of the pages. At the end of the book is a list of 133 questions dealing with the material covered. The appendix lists the symbols, constants, and Greek letters employed.

*Using and Managing Soils.* By A. F. GUSTAFSON. McGraw-Hill Book Company, Inc., New York, 1948. Pp. 420, figs. 190. Price \$2.80.

The outstanding characteristic of this book is its 190 excellent illustrations, which teach much more effectively than the printed word. It is the type of book that, once picked up, cannot be laid down until the reader has leafed it through. The several chapters deal with getting acquainted with the soil, selecting land for farming and country living, tilling and managing crop soils, controlling water and soil erosion, managing acid and alkali soils, keeping up organic matter, conserving farm manures, growing green manures, selecting fertilizers, planning crop rotations, managing pasture, garden, fruit, and lawn soils, and keeping land productive over the years. The author is to be congratulated on leading the way in visual instruction.

THE EDITORS.





# USE OF THERMISTORS FOR MEASURING THE FREEZING POINT OF SOLUTIONS AND SOILS<sup>1</sup>

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*U. S. Department of Agriculture*

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Useful information on the thermodynamic condition of water in solutions, suspensions, and various porous materials may be obtained from freezing point determinations. Sensitive thermometers such as the Beckmann and Heidenhain are commonly used for these measurements. Bodman and Day (3, 4), who used thermocouples for their freezing point measurements, have pointed out some of the disadvantages of mercury-in-glass thermometers. It is difficult, however, to avoid trouble with stray thermal electromotive forces in circuits designed for precise temperature measurements with thermocouples. Thermistors for use as resistance thermometers have recently become commercially available, and the application of these units to routine measurement of the freezing point of solutions is described in this paper.

## TEMPERATURE MEASUREMENT WITH THERMISTORS

Thermistors<sup>3</sup> consist of small beads or plates of semiconducting material with metallic electrodes attached. Electrically, they are useful because of their high negative coefficient of electrical resistance and find many applications in electronic circuits. The high temperature coefficient of resistance makes these units particularly suitable for use as resistance thermometers. Various sizes and shapes of units are available, and different kinds of semiconductors are employed (2). Apparently the semiconducting material used in the units which were designed primarily for temperature measurements has a relatively constant and reproducible relation between resistance and temperature. Table 1 shows a series of readings of the resistance of the Type 14-B Thermistor taken at the ice point. Thermistor No. 1 was immersed in a tube of mercury along with two Heidenhain thermometers, which were simultaneously read. The room temperature and the depth of immersion were kept approximately constant, but no stem corrections were calculated for the thermometer readings. The lower part of the table gives another comparison between the thermometer readings at the ice point and the resistance of another Thermistor unit. These data indicate that the relation of resistance to temperature for the 14-B Thermistor is good enough for relatively precise temperature measurements.

<sup>1</sup> Contribution from the U. S. Regional Salinity Laboratory, Bureau of Plant Industry, Soils and Agricultural Engineering, Agricultural Research Administration, U. S. Department of Agriculture in cooperation with the eleven Western States and the Territory of Hawaii.

<sup>2</sup> Principal soil scientist and junior soil scientist.

<sup>3</sup> "Thermistor" is the trade name for the units which were developed at the Bell Telephone Laboratories and are manufactured by the Western Electric Company.

The Type 14-B Thermistor consists of a cylindrical glass envelope approximately 2 inches long and 0.10 inch in diameter at the large end, which contains the bead of semiconducting material. At the opposite end, tinned wire leads are brought out for making electrical connections. The electrical characteristics as given by the manufacturer are as follows: The resistance at 50°C. is approximately 820 ohms, at 25°C. it is nominally 2,000 ohms, and at 0°C. it is approximately 5,700 ohms. The temperature coefficient of resistance at 25°C. is approximately  $-0.04$  ohm per ohm per degree centigrade. The maximum continuous power rating is 100 milliwatts, and the maximum continuous ambient temperature is 300°C. The thermal time constant in free air is approximately 25 seconds

TABLE 1

*Simultaneous readings of thermometers and Type 14-B Thermistors at the ice point*

DATE	HEIDENHAIN THERMOMETER READINGS		RESISTANCE, THERMISTOR NO. 1
	1	2	
	°C.	°C.	ohms
October 3, 1947.....	0.130	0.178	6077.5
October 7, 1947.....	0.124	0.160	6077.2
October 9, 1947.....	0.125	0.160	6077.6
October 10, 1947.....	0.127	0.159	6077.2
October 11, 1947.....	0.118	0.148	6077.5
October 13, 1947.....	0.128	0.170	6077.1
October 14, 1947.....	....	....	6077.2
Standard Deviation.....	0.004	0.010	0.45*
			THERMISTOR NO. 1
November 10, 1947.....	0.134	....	6425.2
November 21, 1947.....	0.130	....	6425.3
January 7, 1948.....	0.134	....	6425.5
January 15, 1948.....	0.133	....	6425.4

\* Corresponding to 0.0015°C.

and in water is 2 seconds<sup>4</sup>. Each Thermistor must be individually calibrated for use as a resistance thermometer.

The Wheatstone bridge used by the writers for measuring resistance during freezing point measurements is shown in figure 1. The bridge arms R1 and R2 were 1,000 ohms each. R3 is a six-dial resistance box reading to 11,111.1 ohms in steps of 0.01 ohm. The Thermistor is represented by R4, and R5 is a 100,000-ohm resistance used for decreasing the galvanometer sensitivity during rough adjustment of the bridge. The galvanometer key is normally held in the up position by spring action, and depressing the key gives maximum sensitivity for the fine adjustment of R3. The potential difference applied across the bridge,

<sup>4</sup> The thermal time constant is the time required for a Thermistor to make 63 per cent of the resistance change when it is transferred to a new location at a different temperature.

$V_1$ , is 2 volts from a lead cell battery. The galvanometer is a Leeds and Northrup Type HS 2285a with a sensitivity of 0.048 microvolt per millimeter at 1

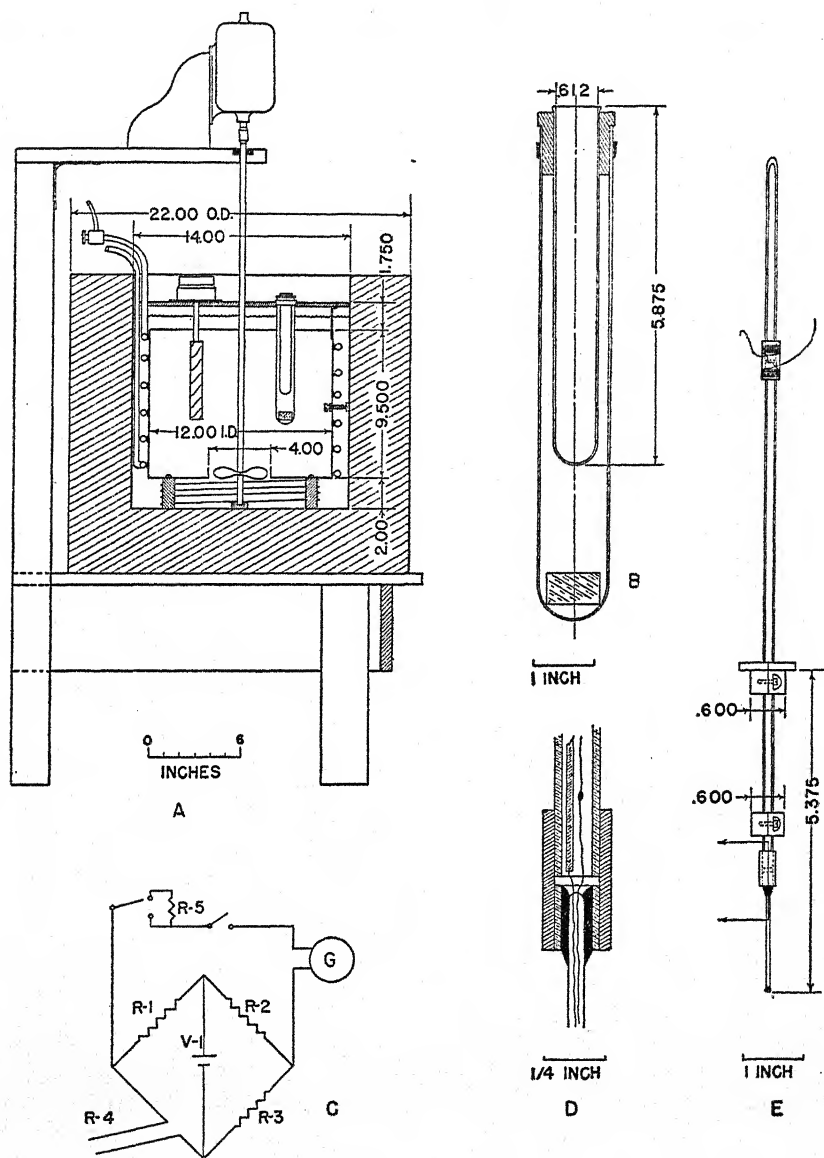


FIG. 1. SKETCHES OF A—FREEZING BATH, B—SAMPLE HOLDER, C—WHEATSTONE BRIDGE WIRING DIAGRAM, D AND E—THERMISTOR MOUNTINGS

meter, period 6.2 seconds, resistance 17.8 ohms, and is used with a 2-meter optical lever. With the Thermistor at the ice point a change of  $R_3$  by 0.1 ohm is detectable. This corresponds to  $0.0003^\circ\text{C}$ .

The arrangement used for containing samples of liquids during freezing is shown in figure 1B. The air jacket is a pyrex glass culture tube 29 mm. outside diameter by 200 mm. long. The sample container is a pyrex culture tube 18 mm. outside diameter and 150 mm. long. The lip of this tube is flared slightly to remove the constriction caused by the fire polishing. The cork spacers shown in the figure were made on a lathe using a grinding attachment. The upper surface of the cork spacers were numbered with India ink before coating with clear lacquer. A tapered supporting ring for the sample unit was made by cutting annular rings  $\frac{5}{8}$  inch outside diameter and  $\frac{3}{8}$  inch inside diameter from  $\frac{1}{16}$ -inch Koroseal sheet. These rings, when heated in boiling water and slipped on the glass tubes, form a tapered sleeve. The holes in the thermostat cover were reamed with a corresponding taper. A piece of lead is inserted in each air jacket to overcome the buoyancy of the thermostat liquid. The tubes can thus be firmly anchored in the cover so they will not move about when the thermostat liquid is rapidly circulated.

The mounting for the Thermistor is shown in the figure. The enlarged section at D indicates how a short length of glass tubing is attached to the upper end of the Thermistor with DeKhotinsky cement. Lead wires consisting of 28-gauge enameled copper magnet wire are soldered to the Thermistor terminals, and one lead is covered with varnished cambric sleeving. A length of glass tubing of the same size as that which is cemented to the Thermistor is then attached with a short piece of Tygon tubing  $\frac{1}{8}$  inch inside diameter by  $\frac{1}{16}$ -inch wall. The lead wires are brought out through a similar Tygon joint higher up. The length of the glass tubing, which serves as a handle, will depend on the use of the Thermistor and, in general, may not need to be as long as the one shown in the figure.

#### FREEZING BATH

Many types of apparatus have been used for obtaining low temperature for freezing point measurements. The freezing bath constructed at the Regional Salinity Laboratory is intended for routine use and is here briefly described, since it contains features not available in commercial thermostats. The stainless steel inner tank shown in figure 1 is insulated with 4 inches of rockwool and is soldered into a galvanized iron outer jacket. A sheet copper baffle is used to control the circulation of the odorless kerosene which serves as the thermostat liquid. The sheet copper baffle as shown in figure 1A is supported on six hardwood legs and has a 4-inch hole in the bottom, in which is inserted a 4-blade impeller. A brass bearing is soldered to the bottom of the tank, and the upper end of the impeller shaft is guided by a ball bearing in the motor support. A flexible coupling is used to make connection to the  $\frac{1}{8}$ -horsepower series wound motor. A 600-watt heater of bare resistance wire is wound on the legs of the baffle. The baffle is spaced and anchored laterally by three screws, one of which is shown in the figure. Brackets extending up from the baffle support the cover for the thermostat, which is made of  $\frac{3}{16}$ -inch presswood and is drilled to accommodate 30 sample tubes and the thermoregulator. The cover is cut on a diameter so that it can be removed without disturbing the motor shaft or refrigerant lines.



The cooling system employs a  $\frac{1}{4}$ -horsepower Freon compressor, which is run continuously during operation of the thermostat. Refrigerant is supplied through a conventional adjustable automatic expansion valve. The evaporation coil consists of six turns of  $\frac{3}{8}$ -inch copper tubing soldered to the outside of the baffle and connected so that the refrigerant enters at the top. The thermostat used is an American Instrument Company bimetallic Type 4-235. This unit is readily adjustable and holds the bath temperature constant to within  $\pm 0.05^\circ\text{C}$ . The thermoregulator contacts control the grid bias of a conventional thermionic relay system for turning the heater on an off, and the slight vibration introduced by the stirring motor causes the heater to operate intermittently from 30 to 60 times per minute.

#### FREEZING POINT OF SOLUTIONS

For the freezing point apparatus and procedures here described, 5-ml. samples of solution are used. The plastic spacers shown clamped to the glass tube in figure 1E are adjusted so that the Thermistor is positioned at the center of the sample.

An undercooling of approximately  $4^\circ\text{C}$ . has been found convenient for soil extracts and plant saps. The procedure for measuring freezing points with this apparatus is as follows: The samples in the sample tubes are installed in the bath. About 3 hours is required to take the bath, containing a set of samples, from room temperature to a low stable temperature ready for freezing. When the bath is already cold,  $1\frac{1}{2}$  to 2 hours is required to cool a new set of samples. The Thermistor is installed in one of the samples, and resistance readings may be made periodically to determine when the samples become cooled. Freezing may be induced in the first sample by agitating the Thermistor or by introducing a seed crystal. Thereafter freezing is induced by crystals adhering to the Thermistor as it is transferred from one sample to the next<sup>5</sup>. If desired, the possibility of error from the mixing of samples by carrying a droplet of solution from one tube to the next during transfer of the Thermistor can be avoided by wiping the Thermistor lightly with absorbent paper tissue.

The course of the freezing is readily indicated by movement of the galvanometer light at low sensitivity, and the temperature of the freezing mixture is usually sufficiently stable that a good bridge balance at high sensitivity can be obtained in about 1 minute. The temperature may drift slowly upward but usually attains a maximum temperature and starts to decrease in 2 or 3 minutes. The maximum temperature is usually recorded as the observed freezing point. To obtain the true freezing point, a correction involving the undercooling and the amount of ice formed during freezing must be applied.

Since the Thermistor has low thermal capacity and low thermal time constant, it is believed that good freezing point values for liquids may be obtained without

<sup>5</sup> Vigorous stirring during freezing is traditional for freezing point measurements. Comparisons were made for several different solutions using Thermistors to obtain freezing points with and without stirring. No consistent differences were obtained, but this finding may not apply to all freezing mixtures.

stirring. The Thermistor should be placed near the center of the sample because loss of heat from the sample begins as soon as freezing starts. For samples of liquid of the size and shape indicated above, no significant difference was obtained when Dewar flasks were substituted for the air-jacketed tubes.

The data in table 2 were obtained on 29 replicates of a 0.200 *N* NaCl solution. The resistance for each sample attained a minimum value, corresponding to the maximum temperature, within approximately 2 minutes after freezing was begun. An elapsed time of about 1 hour was required for the 29 readings. The standard error for this group of measurements was 0.99 ohm, which corresponds to approximately 0.0033°C.

TABLE 2

*Thermistor resistance values\* at the freezing point for replicate samples of NaCl solution*

SAMPLE NUMBER	RESISTANCE	SAMPLE NUMBER	RESISTANCE	SAMPLE NUMBER	RESISTANCE
	<i>ohms</i>		<i>ohms</i>		<i>ohms</i>
1	6639.0	11	6638.8	21	6639.2
2	6635.9	12	6638.3	22	6639.0
3	6636.5	13	6638.6	23	6639.0
4	6637.0	14	6638.8	24	6636.6
5	6636.5	15	6638.2	25	6639.0
6	6638.0	16	6638.9	26	6639.0
7	6638.2	17	6639.1	27	6638.8
8	6638.9	18	6638.6	28	6638.2
9	6638.7	19	6639.2	29	6636.5
10	6637.6	20	6638.2		

\* Standard deviation = 0.99 ohm or 0.0033°C.

#### CALIBRATION

Thermistor resistance readings taken from the bridge can be converted to temperature by graphical or analytical means. In the present case a calibration curve for the Thermistor was obtained by use of a standard thermometer. The Thermistor and the thermometer were immersed in mercury in a test tube which, in turn, was immersed in a Dewar flask filled with crushed ice and equipped with a small motor-driven circulating pump. A zero correction and a stem correction for depth of immersion and room temperature (1, pp. 228-255) were applied to the thermometer readings. The calibration curve was obtained over the temperature range from 0° to -5° C. by successive additions of small amounts of salt to the ice bath. Resistance values over this range were plotted against temperature. Data points thus obtained lie accurately on a smooth curve, and it is possible to convert resistance values to temperature with an interpolation error of the order 0.001 to 0.003°C., depending on the scale used for plotting.

When the ambient temperature is constant, the resistance of a Thermistor will depend on the current flowing through the Thermistor. Consequently, when using Thermistors in a bridge circuit such as shown in figure 1, it is a matter of some importance to maintain the bridge voltage,  $V_1$ , near the value used when the Thermistor was calibrated for use as a resistance thermometer.

It has been shown (1, pp. 159-161) that the ice point is a very good reference standard and that with good technic variations in the temperature at the ice point are of the order of  $0.0001^{\circ}\text{C}$ . With a Type 14-B Thermistor immersed in mercury at the ice point, it was found that over a voltage range near 2 volts, a 0.012-volt change in the bridge voltage caused a change of 0.3 ohm in the Thermistor resistance. This corresponds to  $0.001^{\circ}\text{C}$ .

The lead cell battery used for obtaining the data in table 1 was not new, and the trend in the resistance readings on Thermistor No. 2 is what would be expected with a falling battery voltage. After the battery was charged on January 29, 1948, the Thermistor resistance at the ice point was found to be 6423.6 ohms, which corresponds to a rise of 0.072 millivolt in the battery electromotive force. Nevertheless, with ordinary care, as shown by the data in table 1, the voltage obtainable from lead cell batteries is quite satisfactory for most freezing point work, and measuring the resistance of the Thermistor at the ice point gives a simple check on the condition of the bridge and the calibration of the Thermistor.

TABLE 3

*Equivalent soil moisture stress for Panoche loam\* at three salt levels and four soil moisture tensions*

All data reported in atmospheres

SALINITY	OSMOTIC PRESSURE OF SATURATION EXTRACT	SOIL MOISTURE TENSION						
		0.33	Dif. 0.67	1.00	Dif. 4.00	5.00	Dif. 10.00	15.00
		Soil moisture stress						
No salt added.....	0.16	0.40	0.16	0.55	3.66	4.22	8.89	13.10
Difference.....	4.45	4.26		4.59		4.50		6.36
1st salt level.....	4.61	4.66	0.48	5.14	3.59	8.73	10.73	19.47
Difference.....	4.46	4.95		5.03		5.39		4.90
2nd salt level.....	9.08	9.61	0.56	10.17	3.95	14.12	10.24	24.37

\* RSL Acc. No. 315.

#### FREEZING POINT OF SOILS

The apparatus above described also has been used for measuring the freezing point of soil cores having undisturbed structure. The procedure is very similar to that used for solutions. The cores obtained with the standard King type soil tube are installed in air-jacketed glass sample holders similar to that indicated in figure 1B. Each core is covered by a layer of water-proof Cellophane which is held in place by a cylindrical shaped block of plastic having a central hole and with a funnel shaped upper surface to facilitate insertion of the Thermistor. A central tapered hole is then bored in the soil core, and in the supercooled condition the water in the cores freezes readily in response to the friction and abrasion which occur while inserting the Thermistor.

The procedures for preparing the sample, making the measurement, and applying corrections for undercooling are still under development, but preliminary results look promising. For the sample data shown in table 3, three batches of

soil were made up to a saturated paste by the addition of water while stirring. Salt was added to two batches, thus giving three different salt levels. The osmotic pressures of the solution extracted from the saturated soil at the three salt levels were measured, and they and the differences are listed as the first column of data in the table. Subsamples of the saturated soil from each salt treatment were placed on porous membranes, and solution was extracted until equilibrium was attained at the moisture tensions of 0.33, 1.0, 5.0 and 15.0 atmospheres. These moisture tensions and the differences are given at the top of the table. The uncorrected freezing point depressions<sup>6</sup> for the subsamples were multiplied by 12.06 to give the equivalent soil moisture stress values (that is the sum of osmotic pressure and soil moisture tension) listed in the table. The differences between adjacent stress values in the table are also listed.

Differences in the soil moisture stress values in the columns at constant soil moisture tension are seen to be related to the osmotic pressure differences for the saturation extracts given in the first column of data. Also, differences in the soil moisture stress values at any given salt level are seen to be related to the corresponding soil moisture tension differences given at the top of the table. On the basis of results thus far obtained it appears that it may be possible to develop a rapid routine method for determining the equivalent soil moisture stress in field samples of soil.

#### SUMMARY

The use of a new type of resistance thermometer for measuring the freezing point of solutions and soils is described. Thermistor 14-B, manufactured by Western Electric Company for use as a resistance thermometer, consists of a small bead of semiconducting material which is sealed to appropriate electrodes and is contained in a compact glass envelope. A freezing bath, sample tubes, Thermistor mounting, and bridge circuit are described, and procedure for routine measurement of the freezing point of solutions is given. Preliminary data are also given on freezing point measurements for soils.

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<sup>6</sup> When undercooled soil freezes, ice crystals form throughout the soil mass. This crystal formation in its effect on soil moisture stress is equivalent to a dehydration process, and a correction must be applied to obtain the true freezing point of the soil moisture.

# EFFECT OF VARIOUS FERTILIZER CATIONS AND ANIONS ON SOIL REACTION, LEACHING, NITRIFICATION OF UREA, AND RELATED CHARACTERISTICS IN AN UNCROPPED SOIL<sup>1</sup>

## A REPORT ON WINDSOR LYSIMETER SERIES E

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When nitrogen in the form of commercial fertilizer is added to soils, it is not uncommon for half (6, 7) or more of it to be lost in the drainage water or in other ways. The efficiency of recovery varies widely with the source and the method of application of nitrogen. The soil type, crop grown, other fertilizer elements used, and cultural practices also exert their influence on the uptake of nitrogen by plants. Fundamental information is needed on how much nitrogen and other fertilizer elements are lost through various channels and under a variety of conditions. This kind of information is needed as a basis for practical recommendations that lead to more efficient use of nitrogen, phosphorus, potash, and other plant-food materials in crop production.

One method for obtaining information on the fate of nitrogen in the soil is by use of lysimeters. In 1929 a series of lysimeter experiments was initiated at Windsor, Connecticut (3, 4) to obtain information on soil changes resulting from nitrogen fertilization. Other lysimeter experiments have followed using various sources of nitrogen differing widely in chemical characteristics and rate of availability in the soil (5, 6, 7).

The present lysimeter study involved a comparison of the interaction of various common fertilizer cations and anions in relation to the nitrification of urea (Uramon), to soil reaction and related characteristics, and to the leaching of various constituents from an uncropped soil.

### EXPERIMENTAL CONDITIONS AND PROCEDURE

#### *Lysimeters and soil characteristics*

The general features of the lysimeter installation at Windsor have been described in previous publications (3, 4). In this experiment, a series of 34 cylindrical tanks, 20 inches in diameter and 9 inches deep, of the Windsor lysimeter were

<sup>1</sup> Contribution from the department of soils, Connecticut Agricultural Experiment Station, New Haven, Conn. Part of this material was presented at the Soil Science Society of America meetings, Cincinnati, November 17-20, 1947. An abstract entitled, "Interaction of Various Fertilizer Cations and Anions" was submitted for publication in the Proceedings of the Society.

<sup>2</sup> Grateful acknowledgment is made to the late M. F. Morgan, who initiated this experiment and who also directed it during the initial phases of the work. The writers wish to express their appreciation to S. B. LeCompte, Jr. for his work in maintaining the lysimeters at Windsor during the earlier stages of this study.



used. These tanks occupied the inner row of a series of three rows in the lysimeter. On April 24, 1939, they were filled with Merrimac sandy loam soil taken from a field of the Tobacco Substation at Windsor. Available records show that this field had been in tobacco culture continuously for over 25 years. Soils for other lysimeter studies were also obtained from this same field (3, 4, 5, 6, 7).

Each tank received the equivalent of 123 pounds of oven-dry, thoroughly mixed soil. After this had been well compacted, the depth of the soil in the tanks measured 8 inches and had an apparent specific gravity of 1.35. Other physical and chemical characteristics for the soil are given in table 1. Data on base exchange, Mn, P, pH, N, and C for this original soil are given in tables 8 and 9.

Merrimac sandy loam is a member of the brown podzolic great soil group. The profile is strongly acid and has a weak very fine crumb to single grain structure. It is derived from deep stratified medium sand and gravel deposits of

TABLE 1

*Physical and chemical characteristics of Merrimac sandy loam used in Windsor lysimeter series E at time of collection from the field, 1939*

	<i>per cent</i>		<i>m.e.</i>
Mechanical analysis		Base-exchange per 100 gm. soil	
Total sand.....	69.4	Calcium.....	2.47
Silt.....	20.6	Magnesium.....	0.45
Clay (0.005 mm.).....	10.0	Potassium.....	0.38
Clay (0.002 mm.).....	8.3	Sodium.....	0.04
Moisture equivalent.....	12.0	Exchangeable hydrogen.....	2.70
Nitrogen, total.....	0.115	Total base-exchange capacity...	6.77
Organic carbon.....	1.432	Base saturation ( <i>per cent</i> ).....	60.1
Carbon-nitrogen ratio.....	12.4:1	Active manganese, m.e. per 100 gm.	
pH.....	5.63	soil.....	0.24
Volume weight.....	1.35		

granite, gneiss, and schist materials. Topographically, these soils are located on the extensive glaciofluvial terraces of the Connecticut Valley. The surface soil is grayish brown to brown, the subsoil is light yellowish brown, and the parent materials are light gray or light yellowish brown. The A and B horizons are composed chiefly of sands grading into loose sand and gravel deposits in the C. The entire profile is rapidly permeable to water. This soil is commonly used for tobacco of all three of the types grown in this section (Havana seed, Broad-leaf, and "Shade"). It is also moderately well adapted to potatoes and early vegetable crops.

#### *Plan of treatment*

Choice of materials used in the experiment was based on the need of supplying the four cations Ca, Mg, K, and Na as fertilizer elements. These four bases were each applied in various amounts to duplicate tanks as carbonates, sulfates,

chlorides, and dihydrogen phosphates. Nitrogen in the form of urea (Uramon)<sup>3</sup> was applied to all of the tanks. The rates of application of the bases, depending on the material used, were equivalent to the quantity of nitrates capable of being liberated from 200 pounds of nitrogen per acre applied in the form of Uramon. The amounts of the various elements added in these treatments during the 5 years are summarized in table 2. The table also gives data on the amounts of these elements supplied by precipitation.

TABLE 2  
*Quantity of elements added in fertilizer treatment and by  
rainfall to Windsor lysimeter series E, 1939-1944*

TANK NUMBER	MATERIAL ADDED IN ADDITION TO UREA*	AMOUNT OF ELEMENTS IN MATERIALS ADDED, IN POUNDS PER ACRE							
		Ca	Mg	K	Na	SO <sub>4</sub> -S	Cl	P	N
1- 2	CaCO <sub>3</sub>	1428.5	0	0	0	0	0	0	1000
3- 4	MgCO <sub>3</sub> ·3H <sub>2</sub> O	0	868.5	0	0	0	0	0	1000
5- 6	K <sub>2</sub> CO <sub>3</sub>	0	0	2793.0	0	0	0	0	1000
7- 8	Na <sub>2</sub> CO <sub>3</sub>	0	0	0	1643	0	0	0	1000
9- 10	CaSO <sub>4</sub> ·2H <sub>2</sub> O	1428.5	0	0	0	1143.5	0	0	1000
11- 12	MgSO <sub>4</sub> ·7H <sub>2</sub> O	0	868.5	0	0	1143.5	0	0	1000
13- 14	K <sub>2</sub> SO <sub>4</sub>	0	0	2793.0	0	1143.5	0	0	1000
15- 16	Na <sub>2</sub> SO <sub>4</sub>	0	0	0	1643	1143.5	0	0	1000
17- 18	CaCl <sub>2</sub> ·2H <sub>2</sub> O	1428.5	0	0	0	0	2532.5	0	1000
19- 20	MgCl <sub>2</sub> ·6H <sub>2</sub> O	0	868.5	0	0	0	2532.5	0	1000
21- 22	KCl	0	0	2793.0	0	0	2532.5	0	1000
23- 24	NaCl	0	0	0	1643	0	2532.5	0	1000
25- 26	Ca(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O	1428.5	0	0	0	0	0	2216.0	1000
27- 28	Mg(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub>	0	868.5	0	0	0	0	2216.0	1000
29- 30	KH <sub>2</sub> PO <sub>4</sub>	0	0	2793.0	0	0	0	2216.0	1000
31- 32	NaH <sub>2</sub> PO <sub>4</sub> ·H <sub>2</sub> O	0	0	0	1643	0	0	2216.0	1000
33- 34	None	0	0	0	0	0	0	0	1000
209-210	Rain water	58.6	36.3	37.9	23.6	153.8	163.9	0.65	29.5

\* Urea (Uramon) added to all of the tanks, except 209 and 210. Uramon contains 42 per cent nitrogen.

Analyses were made of the rain water collected during the same period from duplicate open tanks (tanks 209 and 210) on opposite sides of the outer series of rows in the lysimeter. These tanks were also 20 inches in diameter but only 4 inches deep and contained no soil. Crushed trap rock was spread in the areas between the tanks to ensure that no soil would be splashed into any of the tanks during a hard rain. In many cases precipitation was collected in tanks 209 and 210, but the rainfall was so small that water did not percolate through the soil, thereby producing no leachates from the tanks containing soils.

This experiment also involved a study of the acid-base balance of fertilizer

<sup>3</sup> The term "Uramon" is used hereafter in this paper to indicate a commercial form of urea containing 42 per cent nitrogen.

chemicals, with comparisons between corresponding amounts of calcium, magnesium, potassium, and sodium in chloride, sulfate, carbonate, and dihydrogen phosphate forms. In all cases the materials were subject to the activity of equivalent quantities of nitrogen ( $\text{NH}_4\text{-N}$ ,  $\text{NO}_2\text{-N}$ , and  $\text{NO}_3\text{-N}$ ) formed from the nitrification of Uramon. The acidity or basicity of the fertilizer materials used is given in table 3.

TABLE 3

*Acidity or basicity of fertilizer materials used in Windsor lysimeter series E, 1939-1944*

TANK NUMBER	MATERIAL ADDED IN ADDITION TO UREA*	TOTAL MATERIAL ADDED 1939-44*	NET ACIDITY OR BASICITY†	SOIL AT END OF EXPERIMENT	
				Exchange H	pH
		<i>pounds per acre</i>		<i>m.e./100 gm.</i>	
1- 2	CaCO <sub>3</sub>	3706	1920B	3.18	4.98
3- 4	MgCO <sub>3</sub> ·3H <sub>2</sub> O	4942	3650B	2.96	5.33
5- 6	K <sub>2</sub> CO <sub>3</sub>	4936	5914B	3.50	5.00
7- 8	Na <sub>2</sub> CO <sub>3</sub>	3785	2869B	3.25	5.09
9-10	CaSO <sub>4</sub> ·2H <sub>2</sub> O	6149	1786A	4.33	4.18
11-12	MgSO <sub>4</sub> ·7H <sub>2</sub> O	8803	1786A	4.13	4.25
13-14	K <sub>2</sub> SO <sub>4</sub>	6223	1786A	4.10	4.47
15-16	Na <sub>2</sub> SO <sub>4</sub>	5073	1786A	4.58	4.26
17-18	CaCl <sub>2</sub> ·2H <sub>2</sub> O	5249	1786A	4.18	4.46
19-20	MgCl <sub>2</sub> ·6H <sub>2</sub> O	7262	1786A	4.45	4.40
21-22	KCl	5326	1786A	4.53	4.63
23-24	NaCl	4139	1786A	4.33	4.57
25-26	Ca(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O	9006	1786A	5.50	4.51
27-28	Mg(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub>	7821	1786A	4.88	4.74
29-30	KH <sub>2</sub> PO <sub>4</sub>	9724	1786A	5.43	4.69
31-32	NaH <sub>2</sub> PO <sub>4</sub> ·H <sub>2</sub> O	9861	1786A	5.45	4.80
33-34	None	2381	1786A	4.75	4.32
Original soil.....		....	....	2.70	5.63

\* Urea (Uramon) added to all tanks at the rate of 2,381 pounds per acre. Uramon contains 42 per cent nitrogen.

† A—acidic, B—basic.

Under the intensive fertilization practices now widely used for the tobacco, potato, and vegetable crops grown in Connecticut, annual application of nitrogen ranges upward to 200 pounds per acre. A 200-pound-per-acre application of nitrogen in the form of Uramon was therefore made each year to all tanks containing soil.

#### *Experimental methods*

On May 26 of each year, the fertilizer chemicals were thoroughly mixed with the surface 2-3 inches of soil in the tanks. Each treatment was duplicated on opposite sides of the lysimeter. These soils were not cropped but were kept free from weeds by an occasional light cultivation.

Leachates were collected after each period of rainfall causing percolation of water through the soils. The leachates from each tank were measured and samples were taken for immediate determination of nitrate nitrogen. Aliquots were taken of these leachates and were composited into one large sample for each tank for each 6-month period—summer-fall (May 26 to November 25, inclusive) and winter-spring (November 26 to May 25, inclusive). To prevent biological activity during storage, a small amount of toluene (5 ml.) was added to the bottles containing the composite samples.

Ammonia, nitrite, and nitrate nitrogen analyses were made of the composited aliquots at the end of each 6-month collection period. Other constituents analyzed in the leachates are given in tables 5 and 6. The details of the analytical methods used in this experiment are reported elsewhere (3), except for organic matter, nitrite nitrogen, silica, zinc, and iron determinations. The methods used for these determinations are those developed by Schollenberger (10), Spurway (11), Wright (12), Hibbard (2), and Griffin (1), respectively. The pH value was measured with a glass electrode using a 1:1 soil-water ratio.

At the end of the fifth year (May 25, 1944), the soils were removed from the tanks and carefully sampled. They were analyzed for various constituents by the methods mentioned in the preceding paragraph as adapted to soil analyses. The data obtained are presented in tables 8 and 9.

#### RESULTS AND DISCUSSION

##### *Seasonal distribution of leaching*

The average annual precipitation for the 5-year period was 38.57 inches (table 4). This amount was low in comparison with the mean annual rainfall of 45.05 inches<sup>4</sup> for the preceding 83 years at Hartford, Connecticut, 6 miles south of the Windsor lysimeters. At Hartford for this period (1939–1944) the average annual rainfall between May 26 and November 25 was 22.30 inches; from November 26 through May 25 the amount was 22.75. The mean annual rainfall during these two periods from 1939 to 1944 at Windsor was 21.31 and 17.26 inches, respectively. Table 4 gives precipitation and average leachate data for the lysimeter tanks. Precipitation data were obtained from standard rain gauges on top of the lysimeter house.

The 5-year period covered by this experiment was marked by only one season of above-normal rainfall. This wet season (May 26, 1942–May 25, 1943) was followed by one with only 67 per cent of the 83-year average rainfall.

A larger proportion of the rainfall leached through the soil during the second collection period (table 4). Apparently the lower evaporation rate in the second period (4) accounts in part for the larger amounts of leachate for this period. Average evaporation rates at Windsor have been found to be as follows:

	<i>Inches/day</i>
June, July, and August . . . . .	0.112
September, October, and November . . . . .	0.062
December, January, February, and March . . . . .	0.052
April and May . . . . .	0.071

<sup>4</sup> Weather Bureau, U. S. Department of Commerce, Hartford, Conn.

TABLE 4  
Precipitation and leachate data from Windsor lysimeter series E, 1939-1944

MONTH	PRECIPITATION OR LEACHATE	1939-40	1940-41	1941-42	1942-43	1943-44	ANNUAL AVERAGE	WINDSOR 8-YR. AVERAGE
		<i>inches</i>	<i>inches</i>	<i>inches</i>	<i>inches</i>	<i>inches</i>	<i>inches</i>	<i>inches</i>
June	Precipitation	4.37	5.88	4.42	4.28	3.53	4.50	
	Leachate*	0	3.139†	1.617	0.479	0.066	1.06	
July	Precipitation	2.56	3.72	5.64	6.04	2.94	4.18	
	Leachate*	0.618	0.442	1.436	0.959	0.019	0.69	
August	Precipitation	5.62	1.56	2.46	4.66	1.61	3.18	
	Leachate*	0.405	0	0	2.089	0	0.50	
September	Precipitation	2.22	2.57	1.03	4.35	0.76	2.19	
	Leachate*	1.184	0.227	0	1.392	0	0.56	
October	Precipitation	2.20	2.63	1.69	2.66	5.27	2.89	
	Leachate*	2.940	0.336	0	0.984	2.669	1.38	
November	Precipitation	2.81	5.82	3.61	6.22	3.40	4.37	
	Leachate*	0	3.892	2.076	3.136	3.030	2.43	
December	Precipitation	3.02	2.49	2.94	4.15	0.95	2.71	
	Leachate*	0	1.310	1.542	2.977	0	1.16	
January	Precipitation	0.17	2.02	4.38	3.65	0.65	2.17	
	Leachate*	0	1.719	0	0	0.261	0.40	
February	Precipitation	1.19	1.98	2.10	1.15	1.35	1.55	
	Leachate*	0	0	1.014	0	0	0.20	
March	Precipitation	4.97	1.40	7.39	3.25	4.41	4.28	
	Leachate*	2.027	0	5.438	2.520	2.154	2.43	
April	Precipitation	5.62	1.11	0.66	2.98	3.58	2.79	
	Leachate*	6.035	0.666	0	0.715	2.888	2.06	
May	Precipitation	4.08	3.45	4.41	4.89	1.93	3.75	
	Leachate*	0	0.795	0.658	1.120	0.041	0.52	
First period May 26-Nov. 25	Precipitation	19.78	22.18	18.85	28.21	17.51	21.31	24.95
	Leachate	5.15	8.04	5.13	9.04	5.78	6.63	
	% prec. leached through soil	26.04	36.25	27.21	32.05	33.01	31.11	
Second period Nov. 26-May 25	Precipitation	19.05	12.45	21.88	20.07	12.87	17.26	20.51
	Leachate	8.06	4.49	8.65	7.33	5.34	6.77	
	% prec. leached through soil	42.31	36.06	39.53	36.52	41.49	39.22	
Both periods	Precipitation	38.83	34.63	40.73	48.28	30.38	38.57	45.46
	Leachate	13.21	12.53	13.78	16.37	11.12	13.40	
	% prec. leached through soil	34.02	36.18	33.83	33.90	36.60	34.74	

\* Average leachate for lysimeter tanks 1-34.

† May 28, 1940-June 30, 1940.



TABLE 5

Total amounts of various constituents obtained in leachate  
from Windsor lysimeter series E, 1939-1944

TANK NUMBER*	PERIOD†	AMOUNT OF CONSTITUENTS LEACHED, IN POUNDS PER ACRE													
		Ca	Mg	K	Na	Al	N‡	HCO <sub>3</sub>	SO <sub>4</sub> -S	Cl	P	SiO <sub>2</sub>	C	Mn	Fe Zn
1- 2	L-1	1528	110	151	36	2	1092	236	77	36	0.2	73	125	1.1	5 121
	L-2	167	19	48	9	2	65	216	71	33	0.7	41	198	0	3 112
	Total	1695	129	199	45	4	1157	452	148	69	0.9	114	323	1.1	8 233
3- 4	L-1	917	557	141	28	1	1127	245	92	41	0.2	67	123	1.2	6 111
	L-2	95	76	45	8	4	59	242	78	37	1.1	43	216	0	7 120
	Total	1012	633	186	36	5	1186	487	170	78	1.3	110	339	1.2	13 231
5- 6	L-1	919	101	1117	45	3	1091	364	87	54	1.4	65	375	1.9	9 86
	L-2	87	20	314	8	4	72	308	78	37	3.6	45	420	0	18 101
	Total	1006	121	1431	53	7	1163	672	165	91	5.0	110	795	1.9	27 187
7- 8	L-1	627	87	150	1128	3	1105	782	108	46	3.1	68	414	0.6	13 69
	L-2	51	17	33	217	6	67	452	63	35	9.4	46	640	0	21 66
	Total	678	104	183	1345	9	1172	1234	171	81	12.5	114	1054	0.6	34 135
9-10	L-1	2124	127	279	40	6	1090	167	811	41	0.3	78	57	42.0	6 222
	L-2	349	38	73	9	3	54	141	269	37	0.3	41	58	10.0	2 149
	Total	2473	165	352	49	9	1144	308	1080	78	0.6	119	115	52.0	8 371
11-12	L-1	1240	831	245	33	4	1076	256	988	41	0.2	77	84	21.2	4 186
	L-2	137	122	60	7	2	65	160	186	34	0.3	40	101	1.8	1 150
	Total	1377	953	305	40	6	1141	416	1174	75	0.5	117	185	23.0	5 336
13-14	L-1	1311	140	1220	40	5	1114	219	915	42	0.3	78	78	37.0	6 214
	L-2	124	23	413	7	2	60	164	202	39	0.4	38	99	1.7	7 148
	Total	1435	163	1633	47	7	1174	383	1117	81	0.7	116	177	38.7	13 362
15-16	L-1	1159	126	325	1350	5	1083	197	994	45	0.4	80	107	12.1	5 183
	L-2	142	28	69	147	2	71	218	178	40	0.5	42	115	1.7	3 165
	Total	1301	154	394	1497	7	1154	415	1172	85	0.9	122	222	13.8	8 348
17-18	L-1	2436	133	202	40	5	1007	202	54	2465	0.4	77	186	66.1	6 214
	L-2	138	14	47	8	2	52	183	68	59	0.6	40	100	1.4	5 127
	Total	2574	147	249	48	7	1059	385	122	2524	1.0	117	286	67.5	11 341
19-20	L-1	1297	855	220	34	4	989	258	47	2477	0.3	80	163	46.8	5 183
	L-2	79	69	47	8	2	54	212	70	65	0.8	40	177	1.3	4 115
	Total	1376	924	267	42	6	1043	470	117	2542	1.1	120	340	48.1	9 298
21-22	L-1	1367	143	1430	42	4	1065	199	56	2489	0.7	69	205	72.9	8 260
	L-2	64	25	263	7	4	58	226	67	66	2.5	40	174	1.0	17 125
	Total	1431	168	1693	49	8	1123	425	123	2555	3.2	109	379	73.9	25 385

\* See table 3 for materials added.

† L-1 = first period, summer-fall (May 26-November 25).

L-2 = second period, winter-spring (November 26-May 25).

‡ Total N—NH<sub>4</sub>-N; NO<sub>3</sub>-N; and NO<sub>2</sub>-N.

TABLE 5—Continued

TANK NUMBER*	PERIOD†	AMOUNT OF CONSTITUENTS LEACHED, IN POUNDS PER ACRE														
		Ca	Mg	K	Na	Al	N‡	HCO <sub>3</sub>	SO <sub>4</sub> -S	Cl	P	SiO <sub>2</sub>	C	Mn	Fe	Zn
23-24	L-1	1199	116	227	1342	1	985	261	78	2497	0.4	66	238	38.5	5	193
	L-2	71	14	46	124	3	58	279	58	68	1.8	41	118	0.9	5	150
	Total	1270	130	273	1466	4	1043	540	136	2565	2.2	107	356	39.4	10	343
25-26	L-1	1457	131	170	42	2	1067	364	94	50	14.6	116	246	9.1	3	95
	L-2	157	26	50	12	2	47	285	54	35	26.0	54	341	0.3	4	128
	Total	1614	157	220	54	4	1114	649	148	85	40.6	170	587	9.4	7	223
27-28	L-1	922	597	161	38	2	1160	444	106	41	36.2	106	507	1.9	7	63
	L-2	91	99	55	10	4	46	305	60	40	57.8	54	569	0	7	78
	Total	1013	696	216	48	6	1206	749	166	81	94.0	160	1076	1.9	14	141
29-30	L-1	938	122	1142	35	2	1169	459	112	38	92.2	125	384	11.3	8	87
	L-2	65	34	340	9	4	51	271	59	42	85.8	53	493	0	9	97
	Total	1003	156	1482	44	6	1220	730	171	80	178.0	178	877	11.3	17	184
31-32	L-1	599	103	153	1093	2	1117	529	119	37	171.0	113	405	0.9	13	55
	L-2	44	17	31	199	4	57	340	58	36	101.7	58	461	0	9	85
	Total	643	120	184	1292	6	1174	869	177	73	272.7	171	866	0.9	22	140
33-34	L-1	1219	114	193	38	3	1018	211	56	41	1.4	78	97	18.5	4	136
	L-2	145	24	60	10	2	77	183	70	32	0.5	39	130	1.2	3	115
	Total	1364	138	253	48	5	1095	394	126	73	1.9	117	227	19.7	7	251
Average																
1- 8 CO <sub>3</sub> group		1098	247	500	370	6	1169	711	163	80	4.9	112	628	1.2	20	196
9-16 SO <sub>4</sub> group		1647	359	671	408	7	1153	380	1136	80	0.7	118	175	31.9	9	354
17-24 Cl group		1663	342	620	401	6	1067	455	124	2546	1.9	113	340	57.2	14	342
25-32 PO <sub>4</sub> group		1068	282	525	359	5	1178	749	165	80	146.3	170	851	5.9	15	172
33-34 Urea alone		1364	138	253	48	5	1095	394	126	73	1.9	117	227	19.7	7	251

The data in table 4 show that on the average both precipitation (1.55 inches) and leaching (0.20 inches) were least during February. The highest average monthly precipitation occurred in June (4.50 inches) followed closely by November (4.37 inches) and March (4.28 inches). The maximum leaching (2.43 inches), however, occurred during November and March. The relatively low amount of leachate obtained during June (1.06 inches) may be attributed to the comparatively high evaporation rate for June, 0.112 inch per day, in comparison with 0.052 inch per day for March and 0.062 for November.

*Comparison of leachate obtained with previous lysimeter studies*

The average amount of precipitation percolating through the soil in this experiment compares favorably with the two previous 5-year studies using the same lysimeters and conducted under similar uncropped conditions. For the period reported in this paper, 1939-1944, the amount of precipitation leached

TABLE 6

*Total nitrogen fractions in the leachate obtained from Windsor lysimeter series E, 1939-1944*

TANK NUMBER*	PERIOD†	N FRACTIONS, IN POUNDS/ACRE			TANK NUMBER	PERIOD	N FRACTIONS, IN POUNDS/ACRE		
		NO <sub>3</sub> -N	NH <sub>4</sub> -N	NO <sub>2</sub> -N			NO <sub>3</sub> -N	NH <sub>4</sub> -N	NO <sub>2</sub> -N
1- 2	L-1	1058	15	19	19-20	L-1	917	70	2
	L-2	49	4	12		L-2	40	6	8
	Total	1107	19	31		Total	957	76	10
3- 4	L-1	1098	10	19	21-22	L-1	938	125	2
	L-2	43	6	10		L-2	42	5	11
	Total	1141	16	29		Total	980	130	13
5- 6	L-1	1044	12	35	23-24	L-1	937	45	3
	L-2	56	6	10		L-2	41	5	12
	Total	1100	18	45		Total	978	50	15
7- 8	L-1	1069	7	29	25-26	L-1	1035	27	5
	L-2	58	6	3		L-2	41	5	1
	Total	1127	13	32		Total	1076	32	6
9-10	L-1	1035	54	1	27-28	L-1	1100	43	17
	L-2	44	9	1		L-2	40	5	1
	Total	1079	63	2		Total	1140	48	18
11-12	L-1	1003	64	9	29-30	L-1	1124	35	10
	L-2	51	6	8		L-2	44	6	1
	Total	1054	70	17		Total	1168	41	11
13-14	L-1	997	115	2	31-32	L-1	1074	29	14
	L-2	47	6	7		L-2	49	7	1
	Total	1044	121	9		Total	1123	36	15
15-16	L-1	1037	40	6	33-34	L-1	979	36	3
	L-2	51	8	12		L-2	57	11	9
	Total	1088	48	18		Total	1036	47	12
17-18	L-1	925	80	2	<i>Average</i>				
	L-2	34	9	9	1- 8 CO <sub>2</sub> group		1119	16	34
	Total	959	89	11	9-16 SO <sub>4</sub> group		1066	75	12
					17-24 Cl group		969	86	12
					25-32 PO <sub>4</sub> group		1127	39	12
					33-34 Urea alone		1036	47	12

\* See table 3 for materials added.

† L-1 = first period, summer-fall (May 26-November 25).

L-2 = second period, winter-spring (November 26-May 25).

through the soil was 34.7 per cent of the total precipitation. For the 1929-1934 period, the amount of leachate was 41.5 per cent of the total precipitation (3); during the 1934-1939 period, the leachate obtained represented 40.4 per cent

of the total precipitation (7). The average annual precipitation for the three periods mentioned was 38.57, 35.96, and 46.65 inches, respectively.

The amount of precipitation recovered as leachate from cropped lysimeter tanks containing soils 20 and 30 inches deep was less than that obtained from 8-inch fallow lysimeter tanks. The average amount of leachate obtained for the 20-inch tanks at Windsor cropped to one "shade" tobacco plant per tank was 33.3 per cent of the 40.97 inches precipitation occurring during the 11-year period of the study, 1929-1940 (5). In another lysimeter experiment (6) at Windsor, it was found that in tanks with soils 30 inches deep planted to tobacco followed by an oat cover crop, the percolate obtained amounted to 29.7 per cent of the average annual precipitation for the 10-year period, 1931-1941. In this same experiment, but in 30-inch tanks kept fallow, the percolate amounted to 41.1 per cent of the precipitation.

The sandy loam soil in the shallow 8-inch lysimeter tanks evidently retained little soil moisture. With increase in depth of soil, higher amounts of moisture probably would be retained under fallow conditions, but under cropping, the amount used by the plant decreases the total amount available for removal from the soil by leaching. The significance of the amount of water removed by plants from soil is brought out by a comparison of the 30-inch cropped tanks with the 30-inch fallow tanks. In the 30-inch tanks with fallow soils, no water is used by plants and about 11 per cent (4.8 inches) more percolate is obtained.

#### *Seasonal distribution of nitrogen losses by leaching*

The most striking thing about the leaching of nitrogen is that only about 5 per cent of the total amount (table 5) was leached during the second period (November 26-May 25). This held true for all of the treatments. The fact that the fertilizer materials, including Uramon, were added to the tanks on May 26 of each year undoubtedly accounts for the large difference in amounts of nitrogen leached during the two periods. Evidently nitrification of Uramon was very favorable during summer, and little unnitrified Uramon remained. In view of precipitation and leaching data (table 4) removal of more materials from the soil would be expected during the first period. The data in table 4 show that about 55 per cent of the rainfall occurred during this period. Although about the same amount of water leached through the soil during each period, more materials would be expected in the soil solution the first period because of more favorable conditions for physical, chemical, and microbiological activity.

Seasonal temperatures cannot be neglected as a factor in producing the large differences in nitrogen found in the leachates. The average growing season ranges from April 19 to October 18 (8). Temperature conditions during most of the second leaching period are extremely unfavorable for the nitrification of materials by soil organisms.

The data in table 6 show that most nitrification activity takes place from May 26 to November 26. Table 7 throws additional light on the production of nitrates by the nitrification of Uramon. In table 7 only the period from May 26 to November 26 is included. The original data have been grouped into 2-month

intervals, namely, May 26 to August 1, August 1 to October 1, and October 1 to November 26.

TABLE 7  
Average total losses of nitrates, by selected intervals\*, from  
Windsor lysimeter series E, 1939-1944  
In pounds per acre

Comparison of nitrate nitrogen losses by anion groups										
Treatment.....	CARBONATE GROUP					SULFATE GROUP				
	CaCO <sub>3</sub>	MgCO <sub>3</sub> ·3H <sub>2</sub> O	K <sub>2</sub> CO <sub>3</sub>	Na <sub>2</sub> CO <sub>3</sub>	Aver.	CaSO <sub>4</sub> ·2H <sub>2</sub> O	MgSO <sub>4</sub> ·7H <sub>2</sub> O	K <sub>2</sub> SO <sub>4</sub>	Na <sub>2</sub> SO <sub>4</sub>	Aver.
Tank number.....	1-2	3-4	5-6	7-8		9-10	11-12	13-14	15-16	
May 26 to Aug. 1..	48.7	50.7	46.0	54.2	49.9	31.7	29.7	27.3	30.6	29.8
Aug. 1 to Oct. 1...	130.1	137.8	132.6	141.1	135.4	124.3	120.4	122.7	120.8	122.0
Oct. 1 to Nov. 26..	220.5	222.7	214.5	224.3	220.5	200.4	200.4	198.5	206.5	201.4
Treatment.....	CHLORIDE GROUP					PHOSPHATE GROUP				
	CaCl <sub>2</sub> ·2H <sub>2</sub> O	MgCl <sub>2</sub> ·6H <sub>2</sub> O	KCl	NaCl	Aver.	Ca(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O	Mg(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub>	KH <sub>2</sub> PO <sub>4</sub>	NaH <sub>2</sub> PO <sub>4</sub> ·H <sub>2</sub> O	Urea
Tank number.....	17-18	19-20	21-22	23-24		25-26	27-28	29-30	31-32	33-34
May 26 to Aug. 1..	23.2	25.4	25.6	27.4	25.4	33.4	46.2	43.0	43.4	26.8
Aug. 1 to Oct. 1....	110.4	114.6	112.6	119.0	114.1	130.2	152.9	158.7	133.4	105.2
Oct. 1 to Nov. 26..	180.4	183.9	183.2	190.1	184.4	212.5	227.1	232.6	221.6	197.8

Comparison of nitrate nitrogen losses by cation groups

Treatment.....	CALCIUM GROUP					MAGNESIUM GROUP				
	CaCO <sub>3</sub>	CaSO <sub>4</sub> ·2H <sub>2</sub> O	CaCl <sub>2</sub> ·2H <sub>2</sub> O	Ca(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O	Aver.	MgCO <sub>3</sub> ·3H <sub>2</sub> O	MgSO <sub>4</sub> ·7H <sub>2</sub> O	MgCl <sub>2</sub> ·6H <sub>2</sub> O	Mg(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub>	Aver.
Tank number.....	1-2	9-10	17-18	25-26		3-4	11-12	19-20	27-28	
May 26 to Aug. 1.....	48.7	31.7	23.2	33.4	34.2	50.7	29.7	25.4	46.2	38.0
Aug. 1 to Oct. 1.....	130.1	124.3	110.4	130.2	123.8	137.8	120.4	114.6	152.9	131.4
Oct. 1 to Nov. 26.....	220.5	200.4	180.4	212.5	203.4	222.7	200.4	183.9	227.1	208.5
Treatment.....	POTASSIUM GROUP					SODIUM GROUP				
	K <sub>2</sub> CO <sub>3</sub>	K <sub>2</sub> SO <sub>4</sub>	KCl	KH <sub>2</sub> PO <sub>4</sub>	Aver.	Na <sub>2</sub> CO <sub>3</sub>	Na <sub>2</sub> SO <sub>4</sub>	NaCl	NaH <sub>2</sub> PO <sub>4</sub> ·H <sub>2</sub> O	Aver.
Tank number.....	5-6	13-14	21-22	29-30		7-8	15-16	23-24	31-32	
May 26 to Aug. 1.....	46.0	27.3	25.6	43.0	35.5	54.2	30.6	27.4	43.4	38.9
Aug. 1 to Oct. 1.....	132.6	122.7	112.6	158.7	131.6	141.1	120.8	119.0	133.4	128.6
Oct. 1 to Nov. 26.....	214.5	198.5	183.2	232.6	207.2	224.3	206.5	190.1	221.6	210.6

\* First period (summer-fall; May 26 to Nov. 26) of the experiment subdivided into 2-month subperiods.

It should be explained that the totals for nitrates in table 6 cannot be expected to agree exactly with the nitrate totals in table 7. In table 6 the nitrate nitrogen was determined on the composited samples at the end of the 6-month period,



whereas in table 7 the nitrates reported were determined on the leachates obtained after every rain producing leaching.

Comparison of amounts of nitrate nitrogen produced for each 2-month period with amounts of percolate obtained during these same periods (table 4) shows that the amount of water passing through the soil influences the amount of nitrates caught in the leachate.

Probably one factor accounting for the high amount of nitrate nitrogen produced and caught in the leachate during the last 2-month period (October 1–November 25) can be attributed to the large amount of water percolating through the soil for this time interval (table 4) in comparison with the other periods. Any nitrate nitrogen retained in the soil from the previous 2-month period would be subjected to vigorous leaching action. This view is supported by the fact that only 1.06 inches of percolate was caught from August 1 to October 1, whereas 4.81 inches was caught from October 1 to November 26.

*Seasonal distribution of losses of various other constituents from the soil*

Calcium, magnesium, potassium, sodium, and manganese were leached in far greater amounts during the first period (May 26–November 25) than during the second period, in many cases being more than 90 per cent of the total amounts leached (table 5). As in the case of nitrogen, these results can be attributed largely to the fact that the soils were fertilized at the start of the first period.

Part of the greater amounts of these elements found in the percolates can also be attributed to the higher amounts of rainfall for the first period in comparison with the second period. As in the case of nitrogen, seasonal variations in precipitation would also be expected to cause differences in the amount of these bases leached.

Again, seasonal temperature differences for each period evidently had more influence on the amount leached than did the volume of water. It might be expected that the temperature of the percolating water would have an effect on base-exchange activities in the soil. The higher the temperature, the greater the base-exchange activity. It probably also can be assumed that the higher the soil-water temperature, the greater the solubility of the soil minerals. With increases in temperature would come an increase in activity of soil organisms. Increased activity of soil organisms would mean production of larger amounts of organic acids, which would tend to bring soil minerals into solution. The larger amounts of nitrogen leached during this period certainly suggest increased activity of soil organisms.

In contrast to the cations mentioned in the preceding three paragraphs, the carbonate, sulfate, chloride, phosphate, and silicate anions and the cations carbon, iron, zinc, and aluminum were removed from the soil in greater amounts in many cases during the second period (November 26–May 25) of leaching (table 5). The differences between the amounts removed during each period of leaching were not nearly so great as for the cations Ca, Mg, K, Na, and Mn. When a fertilizer carrier contained the carbonate, sulfate, chloride, or phosphate ion, the leachates from the tanks treated with these respective carriers contained, on the whole, more of the ion in question during the first period of leaching. In

general, the anion groups ( $\text{CO}_3$ ,  $\text{SO}_4$ ,  $\text{Cl}$ ,  $\text{PO}_4$ ) were leached in greatest amounts in order of their solubilities— $\text{Cl}$ ,  $\text{SO}_4$ ,  $\text{PO}_4$ ,  $\text{CO}_3$ . The largest amounts of cations and anions were leached from the soils treated with fertilizers carrying chloride and sulfate; those carrying phosphate and carbonate followed next in order.

Nitrogen applied to the soil as Uramon is first transformed to ammonia, then oxidized to nitrite, then further oxidized to nitrate. In the nitrate form, it is generally conceded that it combines with bases and is used by the plant as a nutrient, is immobilized in the soil, or is leached out. Little, if any, accumulation of nitrates normally occurs in sandy soils, such as the Merrimac, with a sandy texture throughout the profile. Since most of the nitrates leached out of the soil during the first period (table 6) only small amounts remained to combine with some cation, thus probably accounting for the increased outgo of the carbonate, sulfate, chloride, phosphate, and silicate anions during the second period. Evidently in sandy soils to which nitrogenous fertilizers have been applied, cations leach out during the warmer months of the year largely as nitrates, whereas during the winter months they are removed as carbonates, sulfates, chlorides, phosphates, and silicates.

*Leaching of various constituents from the soil*

The removal of various constituents from the soil by leaching for a period of 5 years is summarized in table 5.

As is usually the case, virtually no phosphorus was leached from the soil, except in the phosphate group (tanks 25-32) of fertilizer carriers, where the amount was many times larger than for the other carrier groups. No doubt, the fact that higher amounts of phosphorus were added to the soils treated with the phosphorus carriers accounted for the greater removal of this constituent. The fact that phosphorus may be lost in appreciable amounts may be very important from a practical standpoint. Under certain conditions, particularly where high amounts of phosphorus are applied to sandy soils in the Northeast for the growing of tobacco, potato, and vegetable crops, more phosphorus may be leached from the soil than is usually considered to be the case.

In the phosphate group, the phosphorus outgo was influenced most by sodium, followed by potassium, magnesium, and calcium. This grouping with sodium at the top is to be expected because of the relatively high motility of this cation. In comparison with phosphorus, iron and aluminum were leached in somewhat greater amounts, but the amounts were much less than for calcium, magnesium, potassium, and sodium (table 5).

The amount of zinc found in the leachates as reported in table 5 is abnormally high. Even though the tanks were treated with two coats of asphaltum before the tanks were filled in 1939, some of the asphaltum was removed during the 5 years of the experiment and corrosion had brought zinc into the leachate. High amounts of zinc have also been obtained in other experiments conducted in these lysimeters (3).

Calcium was removed from the soil in the largest amounts in the chloride treatments followed in order by the sulfate, carbonate, and phosphate treatments. Less calcium was leached from the untreated tanks than from the chloride and

sulfate groups. Potassium had a slightly greater effect on the leaching of calcium than did magnesium. The average effect of the sodium group of carriers on the removal of calcium was considerably less. Calculation of the total amount of bases (Ca, Mg, K, Na) removed from the soil (table 5) shows that more calcium (52 per cent) was removed by leaching than any of the other bases applied in the fertilizer treatments, being followed by potassium (22 per cent), sodium (14 per cent), and magnesium (12 per cent).

On the average, more magnesium was leached from the sulfate-treated soils than from any of the other anion groups, being followed by the chloride, phosphate, and carbonate forms. As was to be expected, greater amounts of magnesium were obtained in the leachate where magnesium carriers were used in the soil treatments. The potassium group exerted about the same influence on the leaching of magnesium as did the calcium group; the effect of sodium and urea was about 20 pounds per acre less.

There was little difference in the amount of potassium removed from the soil where the potassium sulfate and potassium chloride carriers were used. These two carriers led the others. This same relationship (sodium sulfate and sodium chloride) held true for sodium (table 5).

Rather large amounts of silica were found in the percolate, and the average highest amounts were removed from the soil treated with the phosphate carriers. About the same amounts of silica were removed under the Uramon treatment as for the other treatments. As would be expected, the largest amounts of sulfur were found in the percolates where sulfur was a constituent of the carrier. This same relationship held true for chloride; the largest amounts found were in the leachate from soils treated with the chloride carriers.

It is interesting to note that the chloride and sulfate carriers produced considerably more manganese in the leachate than did the other carriers. Practically no manganese was obtained from the tanks on which the carbonate materials had been used. It is possible that manganese was picked up in the exchange activity more efficiently by the chlorides and sulfates. Once that manganese was in either of these forms, it would be very soluble. On the other hand, manganese is relatively insoluble as a carbonate or a phosphate.

The greatest amount of bicarbonate in the leachate was found in the soils (tanks 25-32) treated with phosphatic materials (table 5). About 220 pounds less of organic carbon per acre was lost in the carbonate (tanks 1-8) than in the phosphate group. The chloride group followed next, with a total of 340 pounds per acre, and the sulfate group was least with 175 pounds. The highest amount of organic carbon found in the leachate for any of the materials used was 1,076 pounds per acre for the magnesium phosphate fertilizer material. The lowest was for calcium sulfate, with 115 pounds. Uramon was low, with only 227 pounds per acre.

#### *Anion and cation effects on nitrification of Uramon*

None of the anion materials used varied greatly in their effects on nitrification, except that nitrification activity in the chloride group and with Uramon alone was slightly less than in the other groups, as judged by the amount of

nitrogen obtained in the percolate (table 5). It might be expected that the carbonate group with higher pH and basicity (table 3) than other groups would have provided more favorable conditions for nitrification activity. According to the leachate data in table 5, no more nitrification took place in the carbonate than in the other groups. The high amount of chloride in the soil for the chloride group (as indicated by the amounts obtained in the leachate) in comparison with the other groups may have been responsible for the retarded nitrification. The high amount of sulfates in the sulfate group apparently had no toxic effect on the soil organisms.

The relatively low amount of nitrogen appearing in the leachate for Uramon (tanks 33-34) treatment (table 5) cannot be attributed entirely to the low pH of the soil in these tanks (table 8). Soil in tanks 9 and 10 with the  $\text{CaSO}_4$  materials added had a pH of 4.18 at the end of the experiment in comparison with 4.32 for the Uramon treatment. Yet these  $\text{CaSO}_4$ -treated soils produced 1,144 pounds of nitrogen in comparison with 1,095 pounds of nitrogen per acre for the Uramon treatment (table 5). The fact that no fertilizer elements except those contained in Uramon were added to tanks 33 and 34 may indicate that the soil organisms lacked other nutrient elements for optimum activity.

When the various fractions of the nitrogen (table 6) obtained in the leachate are considered, it is seen that nearly all of the nitrogen is in the nitrate form. The highest proportion of nitrate nitrogen was found in the carbonate group (96 per cent) and the lowest in the chloride group (91 per cent). The relatively larger amount of ammonia and nitrite nitrogen produced in the chloride group may be due in part to the effect of the high amount of chlorides present (table 5), indicating less complete nitrification of the Uramon. The lower amount of ammonia nitrogen in the carbonate group suggests that the higher pH and basicity favored rapid transformation to nitrate nitrogen. It appears that nitrification was retarded somewhat by the lower pH and acidity of the other groups, leaving larger residues of ammonia to be subjected to leaching.

The data in table 7 show that the phosphate and carbonate anions exerted the most beneficial influence on nitrification of Uramon to nitrates during the summer and fall seasons; sulfates and chlorides followed next in that order. On the other hand, none of the cations (Ca, Mg, K, Na) show any definite trend in their effects on nitrification of Uramon. The cations all produced about the same amounts of nitrate nitrogen, as judged from the amounts obtained from the leachate. For the entire year, the soils treated with the phosphate group of carriers nitrified more of the Uramon than did those treated with the other carriers, although the difference between the highest (phosphate group) and lowest (chloride group) was only about 110 pounds per acre (table 5).

In a general way, the largest amounts of bicarbonates and organic carbon found in the leachate (table 5), in comparison with the other groups, were found in the phosphate group, indicating that nitrification of Uramon is influenced to a marked degree by the nutrient elements available. This fact is further indicated by the potassium and magnesium phosphate materials, each with about 1,210 pounds of nitrogen nitrified per acre and each bringing down into the leachate about 735 pounds of bicarbonate and 900 to 1,000 pounds of organic carbon.

Other fertilizer materials produced greater amounts of a given cation or anion in the leachate but not such high amounts of nitrogen.

The greater degree of nitrification in the phosphate group of materials suggests that phosphorus is one of the more important and limiting nutrient elements for

TABLE 8  
*Comparison of base-exchange and pH data of original soil with samples at the end of 5 years (1939-1944), Windsor lysimeter series E*

TANK NUMBER*	BASE EXCHANGE PER 100 GM. SOIL AT END OF EXPERIMENT			pH AT END OF EXPERIMENT
	Exchangeable H	Base-exchange capacity	Base saturation	
	<i>m.e.</i>	<i>m.e.</i>	<i>per cent</i>	
1- 2	3.18	5.50	42.3	4.98
3- 4	2.96	5.48	46.0	5.33
5- 6	3.50	5.35	34.5	5.00
7- 8	3.25	5.40	39.8	5.09
Av.....	3.22	5.43	40.7	5.10
9-10	4.33	5.70	24.1	4.18
11-12	4.13	5.38	23.3	4.25
13-14	4.10	6.05	32.2	4.47
15-16	4.58	5.83	21.5	4.26
Av.....	4.28	5.74	25.4	4.29
17-18	4.18	6.03	30.7	4.46
19-20	4.45	6.15	27.7	4.40
21-22	4.53	6.20	27.1	4.63
23-24	4.33	5.87	26.3	4.57
Av.....	4.37	6.06	27.9	4.51
25-26	5.50	7.64	28.0	4.51
27-28	4.88	7.38	34.0	4.74
29-30	5.43	7.65	29.1	4.69
31-32	5.45	7.45	26.9	4.80
Av.....	5.31	7.53	29.5	4.68
33-34	4.75	6.13	22.6	4.32
Original soil.....	2.70	6.77	60.1	5.63

\* See table 3 for materials added.

efficient growth of nitrifying soil organisms. The relatively low amount of nitrogen as well as the small amounts of bicarbonates and organic carbon produced in the soils treated only with Uramon strongly suggests that the limiting factor here was the lack of nutrients for maximum production of nitrogen by soil



organisms. Further evidence that biological activity was more active in the soils treated with the phosphatic materials is indicated by the small amount of exchangeable calcium left in the soil at the end of the experiment (table 9). Of all the soils in this experiment, that treated with magnesium phosphate had

TABLE 9

*Comparison of replaceable bases and other data of original soil with soil samples after removal from tanks May 26, 1944 from Windsor lysimeter series E*

In pounds per acre

TANK NUMBER*	EXCH. Ca	EXCH. Mg	EXCH. K	EXCH. Na	ACTIVE Mn	AVAIL. P	TOTAL P	TOTAL N†	CARBON
1-2	949.8	146.1	200.3	20.0	47.4	402.6	3962	2553	33,099
3-4	1099.6	680.8	211.1	18.2	40.7	449.1	3935	2516	33,689
5-6	462.0	150.0	964.4	23.0	40.0	380.5	3864	2344	32,927
7-8	494.4	117.8	240.8	136.0	56.5	432.1	4036	2418	30,030
Av.....	751.4	273.7	404.1	49.3	46.2	416.1	3949	2458	32,436
9-10	520.5	104.6	149.5	14.9	32.2	380.5	3938	2602	31,700
11-12	538.9	147.3	178.7	9.1	48.8	358.4	4137	2676	31,626
13-14	748.3	96.5	755.2	12.8	40.7	378.1	3582	2615	31,994
15-16	748.0	100.4	186.6	23.3	48.1	338.8	3935	2639	32,093
Av.....	638.9	112.2	317.5	15.0	42.4	363.9	3898	2633	31,853
17-18	520.5	65.8	130.8	11.0	27.5	378.1	3889	2676	31,921
19-20	611.5	180.9	165.5	16.2	48.6	446.8	3938	2504	30,644
21-22	325.3	95.0	801.1	15.7	34.4	461.5	3913	2651	30,939
23-24	325.3	105.8	123.2	35.0	49.3	419.8	3854	2651	33,149
Av.....	445.6	111.9	305.1	19.5	40.0	426.5	3898	2620	31,663
25-26	305.6	128.6	196.9	23.9	77.1	687.4	6277	2688	30,398
27-28	286.3	487.8	200.8	25.5	63.1	660.4	5418	2578	29,490
29-30	351.3	135.3	1375.0	28.5	74.4	650.6	6103	2295	29,369
31-32	325.3	180.9	191.0	149.5	89.1	665.3	6022	2553	29,171
Av.....	317.1	233.1	490.9	56.8	75.9	665.9	5955	2528	29,607
33-34	501.1	123.2	138.7	14.6	46.4	346.2	4019	2529	30,718
Original soil.....	1213.0	134.0	369.2	24.2	108.3	800.3	3970	2823	35,162

\* See table 3 for materials added.

† Total N—NH<sub>4</sub>-N, NO<sub>3</sub>-N, and NO<sub>2</sub>-N.

the least amount of calcium remaining, 286 pounds per acre. Yet this treatment ranked first with the potassium phosphate treatment in the nitrification of Uramon. This low status of exchangeable calcium suggests that soil organisms were probably the most active in the soil treated with magnesium phosphate,

producing organic acids such as carbonic acid which tended to leach bases out of the soil. Also, calcium would be used by soil organisms as part of their food, thereby releasing calcium in a soluble form available for leaching from the soil.

*Effect of materials added on base-exchange properties*

Data on the effect of various fertilizers on the base-exchange properties of the soil used in this experiment are given in tables 8 and 9.

The data in table 8 indicate that, in comparison with the original soil, the use of an acidic source of nitrogen such as Uramon increases the exchangeable hydrogen in the soil regardless of the fertilizer carriers used. The exchangeable hydrogen was increased least by the  $\text{MgCO}_3$  treatment (2.96 m.e.) in comparison with the original soil (2.70 m.e.) and most by the  $\text{Ca}(\text{H}_2\text{PO}_4)_2$  treatment (5.50 m.e.). In general, the increase in exchangeable hydrogen was least for the carbonate fertilizer materials (tanks 1-8), intermediate for the sulfate (tanks 9-16) and chloride materials (tanks 17-24), and greatest for the phosphate fertilizer carriers (tanks 24-32). On the other hand, Uramon (tanks 33-34) did not fall into any of these general groups but was slightly above the chloride group in exchangeable hydrogen.

On first thought, one might expect that the soils to which calcium fertilizer carriers has been applied would have increased least in exchangeable hydrogen at the end of the experiment in comparison with the original soil. In fact, there was no relationship between kind of cation (Ca, Mg, K, Na) used in the fertilizer carrier and exchangeable hydrogen (tables 8, 9, and 10). For the cation fertilizer groups, the average sum of the total exchangeable bases (Ca, Mg, K, Na) was highest for potassium, somewhat less for magnesium, and considerably less for the calcium and sodium groups, and least for Uramon (table 10). The average pH for these groups was also in this same order, except for sodium, which was the same as for magnesium. The average exchangeable hydrogen for all of these cation groups, however, was about the same, although highest for Uramon. There appears to be no relationship between the average amounts of Ca, Mg, K, and Na leached from the soil and the amount of these bases in exchangeable form at the end of the experiment (table 10). This relationship also holds true for the anion groups.

In the case of anions ( $\text{CO}_3$ ,  $\text{SO}_4$ , Cl, and  $\text{FO}_4$  carriers) however, the average total exchangeable bases was greatest for the carbonate anion treatment and least for the chloride anion. In a general way, a decrease in exchangeable bases was followed by a correspondingly general increase in exchangeable hydrogen. This latter statement does not hold true for the Uramon-treated soils, which had the smallest amount of total exchangeable bases (table 10) with the next to the highest increase in exchangeable hydrogen in comparison with the original soil.

It might be expected that the total amount of bases (table 5) lost by leaching would be in inverse proportion to the increase in exchangeable hydrogen in the soils as determined at the end of the experiment (table 8). This relationship, in the case of the anion groups, held true only for the carbonate treatments. In these treatments, on the average, the amount of bases (Ca, Mg, K, Na)

leached was least for all of the fertilizer carriers used, the increase in exchangeable hydrogen over that of the original soil was also the least, but the pH was the highest for the anion materials used (table 10). Although the phosphate group of treatments had the highest increase in exchangeable hydrogen, the amount of bases leached from the soil as a group was about the same as that for the carbonate treatments (table 10). The sulfate and chloride groups, which were intermediate in exchangeable hydrogen increases, led the groups in amount of bases removed from the soil by leaching. The amount of bases leached in the

TABLE 10

*Comparison of average total amounts of cations leached with exchangeable bases, exchangeable hydrogen, and pH of the soils at the end of the experiment in Windsor lysimeter series E (1939-1944) by anion- and cation-treatment groups\**

	AVERAGE AMOUNT OF CATIONS† LEACHED	AT END OF EXPERIMENT		
		Average total exch. bases‡	Average exch. H	Average pH
	lbs./A.	lbs./A.	lbs./A.	
Anion groups				
Carbonate.....	2215	1479	79	5.10
Sulfate.....	3085	1084	105	4.29
Chloride.....	3026	882	107	4.51
Phosphate.....	2234	1098	130	4.68
Cation groups				
Calcium.....	2543	872	106	4.53
Magnesium.....	2281	1215	101	4.68
Potassium.....	2978	1585	108	4.70
Sodium.....	2758	871	108	4.68
Uramon‡.....	1803	778	117	4.32
Original soil.....	....	1740	66	5.63

\* Data summarized from tables 5, 8, and 9.

† Ca, Mg, K, Na.

‡ Contains 42 per cent nitrogen.

Uramon treatment was least for all treatments, but the increase in exchangeable hydrogen was next to the highest.

Lower average amounts of bases (Ca, Mg, K, Na) were leached out of the soils (table 10) receiving the treatments containing magnesium and calcium than those receiving potassium and sodium. The average exchangeable hydrogen was also slightly less for the magnesium and calcium treatments than for the sodium and potassium treatments. The differences in pH can hardly be considered of any significance.

All of the fertilizer materials used decreased the base saturation in comparison with the original soil (table 8). The largest decrease was with the  $\text{Na}_2\text{SO}_4$  carrier, from 60.1 per cent (original soil) to 21.5 per cent. The least decrease,

to 46.0 per cent, was with the  $\text{MgCO}_3$  fertilizer. Comparison of the four groups of anion carriers shows that the percentage base saturation was decreased least for the carbonate group. The base-exchange capacity for the phosphate group was highest for the anion fertilizer carriers and well above that of the original soil (table 8). This phosphate group was also highest for the fertilizer carriers in base-exchange capacity. Uramon fell next to the phosphate group for base-exchange capacity, but this amount was less than that of the original soil. This high status of the phosphate carrier might be explained in part by the smaller amounts of bases removed from the soil by leaching. On the other hand, the carbonate group lost about the same amount of bases by leaching and it had the lowest base-exchange capacity.

#### *Effect of acidic and basic materials on pH*

The effect of basic materials on the maintenance of pH is well brought out in table 3. Although, in this experiment, none of the treatments maintained the original pH of the soil, those treatments which were basic increased less in acidity than did the acidic fertilizer carriers. For the carbonate group, which all had a net basicity according to Pierre's (9) method, the basicity data were in close agreement with the pH data. It is not understood, however, why tanks 5 and 6 with a net basicity of 5,914 pounds per acre should have a pH of 5.00 while tanks 3 and 4 with a net basicity of 3,650 pounds per acre should have a pH of 5.33.

In the sulfate, chloride, and phosphate carriers used the net acidity was 1,786 pounds per acre. The pH of the soils in these tanks varied somewhat, but in every case the pH was lower than for the carbonate group. Furthermore, the pH range for the acid groups is not wide and the values are in fairly good agreement.

#### *Comparison of original soil with soils at the end of the experiment*

In every case the replaceable calcium was less at the end of the experiment than in the beginning (table 9). The phosphate group averaged the lowest in replaceable calcium, and the carbonate group the highest. The exchangeable calcium in the  $\text{MgCO}_3$  treatment nearly equalled that contained in the original soil, but the  $\text{Mg}(\text{H}_2\text{PO}_4)_2$  carrier was the lowest, only 236.3 pounds per acre. No doubt the acidic nature of the Uramon applied contributed substantially to the reduction of exchangeable calcium.

The change in replaceable magnesium during the experiment seemed to follow no definite pattern, except that exchangeable magnesium was materially increased in the soils treated with magnesium materials. The carbonate group of carriers, as an average, had considerably more exchangeable magnesium (273.7 pounds per acre) at the end than in the beginning of the experiment (134.0 pounds per acre). The phosphate group was next in line, with about 233 pounds per acre, followed by the sulfate and chloride groups, 112.2 and 111.9 pounds per acre, respectively (table 9).

Whenever potassium was in the carrier, the amount of exchangeable potassium

increased considerably. This was true also for sodium, but not in such a marked degree as for potassium. This observed action for potassium is to be expected and is in line with the generally known fact that potassium is fixed in soil in varying amounts. Presumably large amounts of potassium have been fixed, and an accumulation of this element has occurred in the soil.

The data in table 9 show that total phosphorus accumulated to the largest extent in the phosphate fertilizer group. For the other carriers, the amount of total phosphorus remained virtually equal to the amounts present in the original soil. Available phosphorus was less for all of the fertilizer carriers in comparison with the amount in the original soil. The phosphate-carrier group, however, had more available phosphorus than the other groups. No doubt the large amounts of phosphorus added in this group accounts for the high amounts of total and available phosphorus.

For all of the fertilizer mediums used, the total nitrogen in the soils at the end of the experiment was slightly less than in the original soil. This relationship also held true for organic carbon. In general, a decrease in organic carbon was followed by a similar decrease in nitrogen. There was no significant difference in the decreases among the fertilizer carrier groups (table 9).

When the input (amount added plus original amount) minus the output (amount leached plus amount at end) of nitrogen is considered, it is found that certain amounts of nitrogen for every treatment were lost and could not be accounted for. The largest average annual loss of nitrogen, 69 pounds per acre, occurred in the soil treated with potassium carbonate while the lowest amount, 7 pounds per acre annually, was obtained in the soils treated with magnesium sulfate. The amounts lost during the 5 years of the experiment are 12 and 1 per cent, respectively, of the amount of nitrogen in the original soil. Considering the pH of the soils, their sandy texture, and the relatively small source of energy material for soil organism activity, one might expect, on the basis of present knowledge, to find no accumulated or fixed nitrogen in these soils.

On another percentage basis, the total losses of nitrogen (345.5 and 35.5 pounds per acre, respectively, for these same treatments) represent a loss of 34 per cent and 3 per cent respectively, of the total amount of nitrogen applied in Uramon and by rainfall during the experiment. These net nitrogen losses compare with the 10 to 20 per cent average losses reported for other lysimeter work (3, 4, 5, 6, 7). The 34 per cent maximum loss of nitrogen for this experiment is less than the 50 per cent maximum loss obtained for one treatment (ammonium sulfate fully neutralized) in lysimeter series D (7) conducted during 1934-1939 in the same tanks as those used in this study.

Another method of calculation is to take the input of nitrogen (3852.5 pounds per acre) as the basis for determining percentage losses. On this basis, the nitrogen lost is 9 per cent for the potassium carbonate treatment and 0.9 per cent for the magnesium sulfate treatment. This method of calculation takes into consideration all of the nitrogen, both in the soil and added, which entered into the experiment.

Undoubtedly, some of the nitrogen losses for this experiment can be explained



by analytical error. Some nitrogen probably was lost by volatilization of ammonia or by the escape of nitrogen gas or oxides of nitrogen. Since losses of nitrogen in these forms were not determined, it is impossible to evaluate the amount or relative importance of each.

#### SUMMARY

A comparison of the interaction of various common fertilizer cations (Ca, Mg, K, Na) and anions ( $\text{CO}_3$ ,  $\text{SO}_4$ , Cl,  $\text{PO}_4$ ) in relation to the nitrification of urea (Uramon), to soil reaction and related characteristics, and to the leaching of various constituents from an uncropped sandy loam soil in a lysimeter experiment conducted for a 5-year period is reported.

About 95 per cent of the nitrogen leached from the soil came through during the first 6 months after the application of fertilizers (May 26–November 25).

Phosphate and carbonate anions exerted the most beneficial influence on the nitrification of Uramon to nitrates; sulfates and chlorides followed next in order. The cations produced no marked differences in their effect on nitrification. Apparently the nitrification of Uramon is influenced to a marked degree by the kind and amount of nutrient elements available. In this experiment, phosphorus appeared to be the limiting element for maximum nitrification of Uramon to nitrates.

None of the treatments in this experiment maintained the original pH of the soil, but those treatments which were basic in reaction increased the soil acidity less than did the acidic fertilizers. Uramon increased the exchangeable hydrogen in the soils regardless of the fertilizer material used with it, the increase being greatest for the phosphate group and least for the carbonate group.

For the cation fertilizer groups, the average total exchangeable bases (Ca, Mg, K, Na) in the soil at the end of the experiment was highest where potassium had been a constituent of the fertilizer material added, somewhat less where magnesium had been applied, and considerably less for the calcium and sodium treatments. The total exchangeable bases was the lowest where Uramon only had been applied. Comparison of the anion carriers showed that the average total quantity of exchangeable bases was greatest for the carbonate anion treatment and least for the chloride treatment.

In every case the replaceable calcium was less at the end of the experiment than in the beginning. Exchangeable magnesium seemed to follow no definite pattern, except that it was materially increased where the soils had been treated with magnesium materials. Whenever potassium was the cation in the carrier, the amount of exchangeable potassium increased considerably in the soil; this was true for sodium to a less marked degree.

Calcium, magnesium, potassium, sodium, and manganese were leached in the greatest amounts (as much as 90 per cent of the total amount leached) during the first 6-month period following fertilizer application (May 26). In contrast to these cations, the carbonate, sulfate, chloride, phosphate, and silicate anions and the cations carbon, iron, zinc, and aluminum were removed in greater amounts in most cases during the second period (November 26–May 25). Since

most of the nitrates leached during the first period, the outgoing cations in the second period would have to combine with some anion other than nitrate, thus accounting for the increased outgo of the carbonate, sulfate, chloride, phosphate, and silicate anions.

In the calcium cation group, calcium was removed from the soil in the largest amounts in the chloride treatments, followed in order by the sulfate, carbonate, and phosphate treatments. In the case of the cations Ca, Mg, K, and Na, in general more calcium (52 per cent of these total cations leached) was removed by leaching than any of the other bases applied in the fertilizer treatments, followed by potassium (22 per cent), sodium (14 per cent), and magnesium (12 per cent).

Slightly more magnesium was leached from the soils treated with the sulfate form of the fertilizer than from those treated with the chloride. The largest amounts of potassium were leached from soils treated with the chloride and the sulfate. This same general relationship held true for sodium.

Little phosphorus was leached from any of the soils, except in the case of the phosphate group of carriers, where the amount was many times larger than for the other carrier groups. The fact that phosphorus may be lost in appreciable amounts from sandy soils in the Northeast may be important from a practical standpoint.

In general, the largest amount of a given constituent (Ca, Mg, K, Na, CO<sub>3</sub>, SO<sub>4</sub>, Cl, PO<sub>4</sub>) was found in the percolate where that constituent was a part of the fertilizer material added to the soil.

The largest amounts of materials (cations and anions) were leached from the soils to which sulfate and chloride fertilizer materials had been applied. Considerably smaller amounts were leached from the soils treated with phosphates and carbonates. In general, the anion groups were leached from the soil in the order of their solubilities.

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# EFFECT OF COPPER FERTILIZATION ON CAROTENE, ASCORBIC ACID, PROTEIN, AND COPPER CONTENTS OF PLANTS GROWN ON ORGANIC SOILS<sup>1</sup>

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The supply of available nutrients within a soil affects the nutritional values as well as the yields of crops produced on that soil. The food value of plants cannot be measured adequately by determining any one organic constituent; it must be determined by measurement of several constituents. In general, a food of high nutritional value is one that is high in proteins, carbohydrates, and vitamins. Perhaps food values can best be measured by actual feeding tests. Such tests do not show, however, which constituents have actually been affected by the fertilizers applied for the crop.

It is the purpose of this paper to report the effect of copper deficiency on the carotene (pro-vitamin A), ascorbic acid (vitamin C), protein, and copper contents of plants.

## REVIEW OF LITERATURE

Recently a few papers have been published on the use of minor elements for improving nutritional quality of crops. In an experiment with turnip greens, Bernstein, Hamner, and Parke (5) found that fertilizers, either in pot cultures or on field plots, did not affect the content of ascorbic acid. These results were obtained in spite of the fact that fertilizer did affect the growth and appearance of the plants. Likewise, there was no appreciable effect of fertilizer on carotene content, except of visibly chlorotic plants growing in sand cultures.

Lyon, Beeson, and Ellis (12) reported that the fruit of tomato plants grown in a complete nutrient solution did not show significant differences in the ascorbic acid and carotene content over those deficient in copper.

Harmer (6) reported that the sugar content of carrots and table beets was appreciably reduced in copper-deficient plants.

Loustalot, *et al.* (9) found a highly significant reduction in the rate of carbon dioxide assimilation in both slightly and markedly copper-deficient leaves of tung trees. They expressed the belief that the apparent decrease in photosynthesis was not primarily associated with the appearance of chlorosis or necrosis of the leaf tissue.

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Orth, *et al.* (14) found that a copper deficiency in oranges affected the chlorophyll content of the leaves. Leaves of trees treated with copper contained 4.6 times as much chlorophyll as did those from untreated trees.

Meiklejohn and Stewart (13) reported that cucumber juice contained a copper protein complex, which was described as ascorbic acid oxidase. This enzyme was much more active catalytically than the same amount of copper in the ionic form ( $\text{CuSO}_4$ ). They believed that their preparation was nearly identical to an enzyme found in potatoes and previously described by Kubowitz (8). This enzyme oxidized polyphenols and in the pure state contained about 0.2 per cent copper. Lovett-Janison and Nelson (10) isolated from crook-neck squash a blue to bluish green enzyme which contained 0.15 per cent copper and was free from peroxidase activity. It catalyzed the oxidation of ascorbic acid. Other copper enzymes purified and described are laccase (1), and polyphenol oxidase (7).

In a study of the effect of minor elements on the enzyme activity of tomato plants, Bailey and McHargue (3) found an interesting relationship between copper concentration in the nutrient solution and oxidase activity in the leaves. Assuming that the plants grown without copper had a relative oxidase activity value of 100, they showed that plants growing in nutrient solutions containing 0.01, 0.05, and 0.1 p.p.m. of copper had a relative value of 110, 122, and 140 respectively. The enzyme invertase was increased markedly in the tomato fruit by increased amounts of copper in the nutrient solution. The amount of peroxidase and catalase activity diminished progressively with increasing copper.

#### EXPERIMENTAL PROCEDURE

In the study of the effect of copper on the carotene, ascorbic acid, protein, and copper contents, plants were grown in the greenhouse and in the field. Ascorbic acid was measured by the 2,6-dichlorophenolindophenol method, as modified by Lucas (11), in which 20 to 30 gm. of plant material was dispersed with a Waring Blendor in 180 to 270 ml. of metaphosphoric acid solution. Carotene was measured by the procedure described by Benne, *et al.* (4). Because of the small amount of growth, especially when no copper was applied, it was sometimes difficult to get representative samples from 3 to 5 gm. of plant material. In such cases, sufficient material was dispersed in acetone with the Waring Blendor. After this was refluxed and filtered, an appropriate aliquot was taken for separation and measurement of the carotene. Protein was measured by determining amino nitrogen in the dried sample (2) and converting by use of the factor 6.25. Copper was determined by the diethyldithiocarbamate method (2).

The samples of field plants to be used for carotene and ascorbic acid measurements were collected in the early morning and analyzed the same day. Moisture content of plants was determined on samples of the green material oven-dried at 98°C. The same general procedure was followed for the carotene analyses of plants grown either in the field or in the greenhouse. No effort was made to determine the moisture content of plants grown in the greenhouse for ascorbic acid analysis, as a representative sample was taken within 5 minutes after the plants were harvested.



Plant samples from the crops grown in the field were collected from experimental plots under investigation since 1942 at the Michigan State College Muck Experimental Farm. The plants were cut at ground level at the normal time of harvest.

The soil for greenhouse study was passed through a  $\frac{1}{4}$ -inch square-mesh wire screen which was coated with asphalt. Crops were grown in equal quantities of the thoroughly mixed soil placed in 2-gallon glazed jars. At intervals the soil was brought to an optimum moisture content with distilled water. Chemically pure nutrients were added to the soil of each jar at the equivalent rate of 2,000 pounds per acre of a 3-9-18 fertilizer. Copper was added as  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ . Each treatment was replicated three times.

#### RESULTS AND DISCUSSION

Table 1 shows the ascorbic acid and carotene contents of fall- and spring-grown spinach. Though the increase in yield caused by copper fertilization was much greater in spring than in fall, the increase in ascorbic acid content resulting

TABLE 1  
*Influence of minor elements on yield and ascorbic acid content of spinach grown in the greenhouse*

TREATMENT	FALL-GROWN		SPRING-GROWN	
	Weight of fresh material	Ascorbic acid*	Weight of fresh material	Ascorbic acid†
	gm.	mgm./100 gm.	gm.	mgm./100 gm.
Control.....	97	57	49	95
Copper.....	123	72	127	102
Cu, Mn.....	114	73	—	—
Cu, Mn, Zn.....	118	71	130	100

\* Differences highly significant over control values.

† Differences not significant.

from the copper treatment was much greater in fall. The spring-grown plants showed no copper-deficiency symptoms. The plants grown in fall without copper developed a mottling and were not so dark green as plants fertilized with copper.

The chemical analyses shown in table 2 are the results obtained from wheat grown in the field. They indicate that copper had little effect on the ascorbic acid content of wheat at two stages of maturity. The only significant difference resulting from the copper treatment was an increase in the carotene content at the preheading stage.

As shown in table 3, the carotene and ascorbic acid contents of field-grown spinach and onions were not markedly affected by copper sulfate treatments. The only apparent effect of the copper was to increase the carotene content of the spinach.

Tables 4 and 5 show the results obtained from growing barley and carrots in the greenhouse on soil from the College Muck Farm. Both crops responded to

copper fertilization. The barley plants growing on soil that did not receive copper were of yellow to yellowish green. The application of 10 pounds of copper sulfate per acre did not entirely eliminate the deficiency symptoms but was

TABLE 2

*Effect of copper on ascorbic acid and carotene contents of wheat grown in the greenhouse*

TREATMENT*	WHEAT† HARVESTED JUNE 9, 1945		WHEAT, PREHEADING† HARVESTED JUNE 30, 1945	
	Ascorbic acid	Carotene	Ascorbic acid	Carotene
	mgm./100 gm.	mgm./100 gm.	mgm./100 gm.	mgm./100 gm.
Control.....	63	4.5	25	1.9
300 CuSO <sub>4</sub> in 1942.....	56	4.6	26	2.8
50 CuSO <sub>4</sub> in 1942.....	58	4.5	27	2.5
50 CuSO <sub>4</sub> in 1942, 1943, 1944, 1945.....	56	4.7	25	2.6

\* CuSO<sub>4</sub> treatments shown at the pound/acre rate.

† Corrected to 90 per cent moisture.

TABLE 3

*Effect of copper on ascorbic acid and carotene contents of field-grown spinach and onions*

TREATMENT*	SPINACH PETIOLE†		GREEN ONIONS† EARLY BULBING STAGE	
	Ascorbic acid	Carotene	Ascorbic acid in tops	Ascorbic acid in bulbs
	mgm./100 gm.	mgm./100 gm.	mgm./100 gm.	mgm./100 gm.
Control.....	71	5.9	26.0	16.6
50 CuSO <sub>4</sub> in 1942.....	74	6.4	24.4	15.1
50 CuSO <sub>4</sub> annually.....	70	6.3	24.8	15.3

\* CuSO<sub>4</sub> treatments shown at the pound/acre rate.

† Corrected to 90 per cent moisture.

‡ Corrected to 91 per cent moisture.

TABLE 4

*Effect of copper sulfate applied to muck soil in pot cultures on yield and carotene and ascorbic acid contents of barley*

TREATMENT*	GREEN WEIGHT PER JAR	ASCORBIC ACID	CAROTENE
	gm.	mgm./100 gm.	mgm./100 gm.
Control.....	63	29.2	4.00
10 CuSO <sub>4</sub> .....	122†	45.1†	5.40†
100 CuSO <sub>4</sub> .....	122†	46.5†	6.60†

\* CuSO<sub>4</sub> treatments shown at the pound/acre rate.

† Differences significantly greater than the results from the control treatment.

equal to the 100-pound application so far as yield was concerned. The carotene and ascorbic acid contents of the barley were significantly increased by the 10-pound-per-acre application of copper sulfate. The larger application of copper

caused a further increase in carotene content but no further increase in ascorbic acid content.

Table 5 shows that the yield and carotene content of carrots were greatly increased by an application of 100 pounds of copper sulfate per acre. The data

TABLE 5  
*Effect of copper sulfate on yield and carotene content of carrots\**  
Fresh material

TREATMENT	DECEMBER 15, 1945		JANUARY 2, 1946		JANUARY 21, 1946	
	Yield	Carotene	Yield	Carotene	Yield	Carotene
	gm.	mgm./100 gm.	gm.	mgm./100 gm.	gm.	mgm./100 gm.
Control.....	24	2.16	104	4.30	126	5.06
100 lbs. CuSO <sub>4</sub> /acre.....	110	3.50	432	6.08	590	5.96

\* Crop planted October 15, 1945.

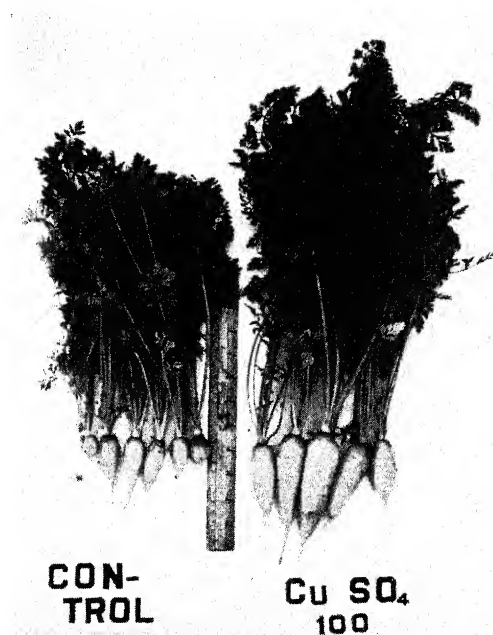


FIG. 1. EFFECT OF COPPER SULFATE ON CARROTS  
Rate of CuSO<sub>4</sub> application, 100 pounds per acre

show that the difference in carotene content effected by copper diminished as maturity advanced. Figure 1 shows the effect of copper fertilization on both tops and roots of carrots.

Tomato fruit harvested from plants receiving copper fertilization did not show any significant differences in ascorbic acid as a result of treatment even though

the yield was increased over 30 per cent. The ascorbic acid values varied between 18.8 and 21.2 mgm. per 100 gm. of fresh fruit.

The data reported in table 6 show that yields, ascorbic acid, and carotene contents of oats, grown in the greenhouse, were greatly increased by applications of copper sulfate, irrespective of the degree of acidity of the muck. The greatest

TABLE 6

*Carotene and ascorbic acid contents of oats grown on organic soil with and without addition of copper sulfate at various pH levels*

pH	FRESH WEIGHT OF CROP PER JAR			ASCORBIC ACID			CAROTENE		
	No copper	Copper added*	Increase due to copper	No copper	Copper added*	Increase due to copper	No copper	Copper added*	Increase due to copper
	gm.	gm.	gm.	mgm./100 gm.	mgm./100 gm.	mgm./100 gm.	mgm./100 gm.	mgm./100 gm.	mgm./100 gm.
3.6	14	102	88	22.5	29.5	7.0	6.50	8.83	2.33
4.6	126	146	20	23.0	36.0	13.0	7.25	8.10	0.85
5.9	143	177	34	26.8	35.0	8.2	8.10	8.52	0.42
7.2	136	192	56	27.2	32.5	5.3	7.15	8.92	1.77
Average.....				24.9	33.2	....	7.25	8.59	....

\* CuSO<sub>4</sub> applied at the rate of 100 pounds per acre.

TABLE 7

*Protein contents of copper-deficient and normal plants  
Oven-dried samples*

CROP	PROTEIN CONTENT		
	Copper-deficient plants	Copper-fertilized plants	Decrease due to copper
	per cent	per cent	per cent
Alfalfa.....	32.6	30.2	7.4
Barley (preheading).....	38.9	27.2	30.1
Oats (preheading).....	33.2	29.4	11.4
Wheat (preheading).....	34.2	32.9	3.8
Wheat grain.....	21.5	19.4	9.8
Sugar beets.....	24.4	19.9	18.4
Tomato fruit.....	15.9	13.9	12.6
Carrot roots.....	19.6	13.2	33.6
Average.....			16.0

response in yield occurred on the unlimed muck where the pH was 3.6. As the pH was raised by liming to 4.6 and 5.9, yield response to the copper seemed to become less and then to increase again at pH 7.2. The same trend was evident in the carotene content, for the greatest increase was obtained at the low soil pH, and the least difference was obtained at the intermediate pH levels. In the case of ascorbic acid, there seemed to be greater differences at the intermediate pH levels.

One of the symptoms of copper deficiency in wheat, oats, and barley is the general chlorosis of the plant. The grain from copper-deficient wheat is pale brown, whereas that from normal plants is dark reddish brown. These symptoms appear similar to nitrogen deficiency. Actually, this malnutritional condition is not due to nitrogen deficiency, for, as shown in table 7, the protein content of copper-deficient wheat grain and plants was found to be exceptionally high. Quick tests by the diphenylamine method for nitrates in the stems or petioles indicated that both normal and copper-deficient plants were adequately supplied with nitrate-nitrogen. Evidently a copper deficiency does not inter-

TABLE 8  
*Effect of copper fertilization on copper contents of various plants*  
Dry-weight basis

CROP	DEGREE OF RESPONSE	COPPER IN PLANTS, P.P.M.	
		Control	Copper sulfate*
Alfalfa†.....	Fair	5	10
Barley (preheading).....	Good	10	14
Carrot roots.....	Good	3	5
Dill seed†.....	Good	6	12
Head lettuce†.....	Good	3	9
Ladino clover†.....	None	7	14
Oats (preheading).....	Good	11	15
Onion bulbs†.....	Fair	2	5
Peppermint†.....	None	8	12
Red clover†.....	None	7	15
Sudan grass.....	Good	5	10
Sugar beets (tops).....	Good	6	7
Spinach.....	Good	8	12
Tomato fruit.....	Fair	4	8
Wheat grain†.....	Good	6	8
Wheat (preheading)†.....	Good	8	12

\* Copper sulfate added at the rate of 100 pounds per acre.

† Crops grown in the field. Data on degree of response for field crops were obtained by Harmer.

fere in the conversion of carbohydrates to proteins. Since the reports of Lous-talot (9) and Harmer (6) show that copper aids in photosynthesis and in formation of simple sugars, the role of copper is probably involved in the early stages of food synthesis.

The data in table 8 compare the copper contents of several crops grown on soils with and without additions of copper sulfate at the rate of 100 pounds per acre. Most of the plants showing copper deficiency contained about 5 p.p.m., and the addition of copper sulfate approximately doubled the copper content. Exceptions to this general observation are the copper contents of oats and barley. These two crops were grown on very acid soils (pH 4.3), whereas other crops analyzed for copper were grown on soil with pH 6.1. On the basis of other in-



vestigations by the author<sup>3</sup>, it is believed that an adequate level of copper in any crop is not a specific figure but is related to the amount of other plant nutrients and organic compounds in the plant.

The conclusion drawn from the chemical analyses of plants deficient in copper is that the carotene and ascorbic acid contents may be appreciably affected. Although the data of Lyon *et al.* (12) and Bernstein *et al.* (5) indicate otherwise, the results of this research indicate that copper deficiency can disturb some organic constituents in the plant. For this reason, feeds and food from copper-deficient plants may be lower in nutritional value as well as in copper. One of the physiological roles of copper is to form a protein enzyme (7, 10) which is specific for the oxidation of ascorbic acid. This study has shown that the increased absorption of copper by plants grown on soil fertilized with copper sulfate does not decrease the ascorbic acid content. Undoubtedly, the plant cell, under certain circumstances, has inhibiting enzymes which counteract the action of the copper enzyme. Only by a breakdown of these inhibiting enzymes, such as is accomplished by aging, cooking, or cell disintegration, does copper exhibit its noted property of destroying ascorbic acid.

#### SUMMARY AND CONCLUSIONS

A study of the effect of copper fertilization in organic soils upon the ascorbic acid, carotene, protein, and copper contents of plants has borne out the following conclusions:

Plants grown in soils deficient in copper contained one fourth to one half as much copper as plants grown on copper-fertilized soil. An adequate level of copper in plants is probably not a specific value, but is related to the composition of other nutrients and organic compounds in the plant.

In greenhouse trials the application of copper to deficient muck soils increased the ascorbic acid content of barley, oats, and fall-grown spinach, but did not affect the ascorbic acid content of spring-grown spinach and tomato fruit. In field-grown crops, onions, spinach, and wheat showed no significant differences in ascorbic acid content.

The application of copper increased the carotene content of greenhouse-grown wheat, spinach, barley, carrots, and oats.

The protein content of plants deficient in copper was found to be abnormally high. This would indicate that copper does not aid in the formation of proteins.

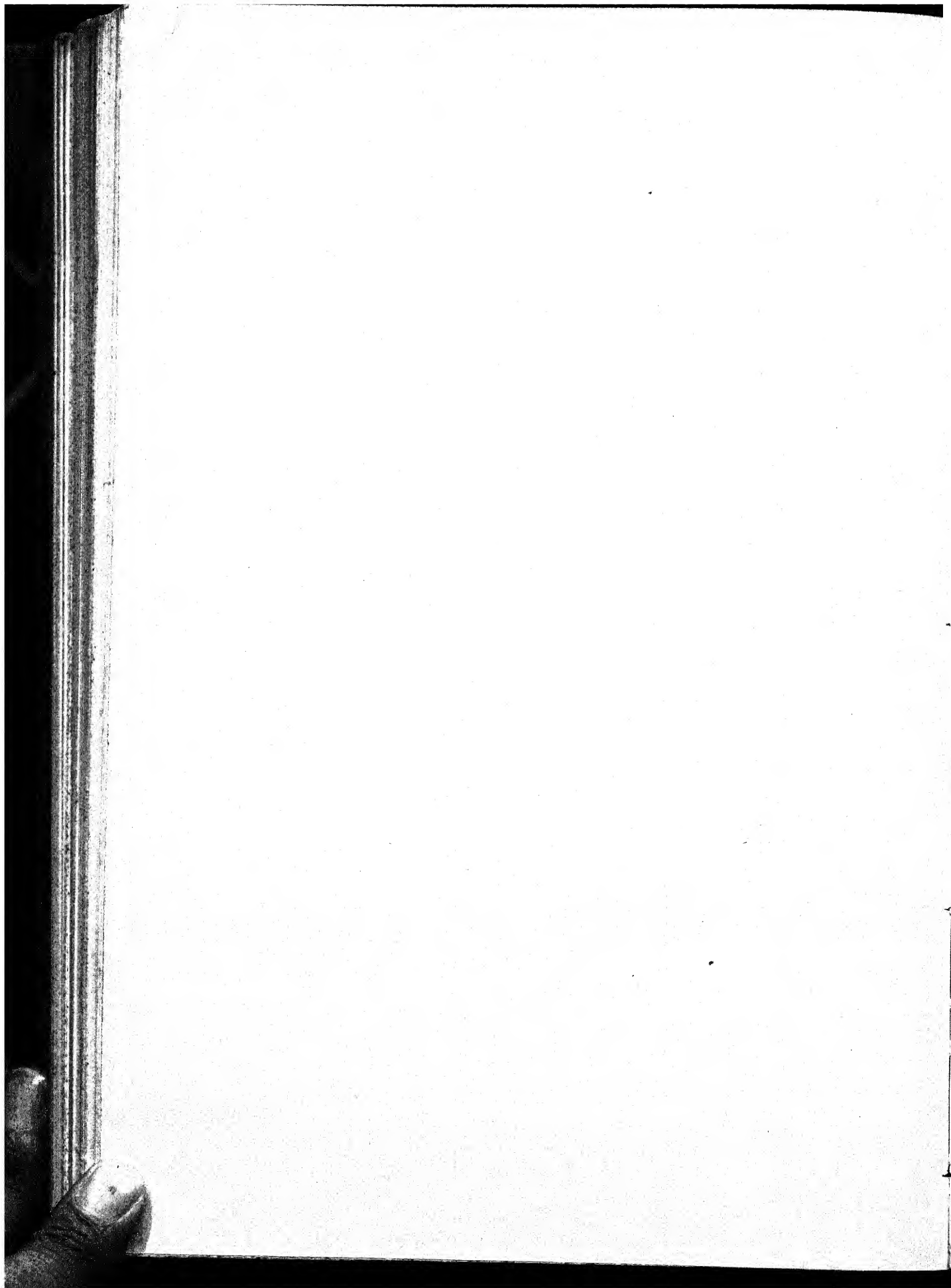
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## EFFECT OF DIFFERENT MULCHES UPON THE NUTRITIVE VALUE OF TOMATOES<sup>1</sup>

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Since the tomato grows satisfactorily in virtually all areas of the United States, it is quite evident that this species of plant tolerates a wide range of temperatures, types of soil, fertilizers, soil acidity, and amounts of sunshine and rainfall. This observation naturally raises a question concerning the ideal conditions for obtaining an optimum production of tomatoes. To the commercial grower, "optimum production" means a high yield of excellent-quality marketable tomatoes. The ultimate consumer and those concerned with human nutrition are primarily interested in tomatoes of highest possible food value, but the tomatoes are actually purchased on the basis of their appearance. Tomatoes are almost universally considered one of the best dietary sources of reduced ascorbic acid. Accordingly, numerous studies have been made of the ascorbic acid content of tomatoes as affected by such factors as varieties, fertilizers, seasons, and amount of sunshine. A survey of the literature revealed little data on the effect of mulches on the nutritive value of tomatoes. The purpose of this study was to accumulate data regarding the effect of this cultural procedure.

### EXPERIMENTAL

#### *Experimental period*

The experiment was of 6 years' duration. With one exception, Servall mulch, which is described later, all controllable conditions were maintained uniform for each of the experimental plots for all 6 years. It was assumed that a 5-year experimental period was of sufficient length to stabilize soil, fertilizer, and cultural conditions enough to justify a comparison of the nutritive value of tomatoes produced. Hence, during the sixth year of the experiment, tomatoes were collected for assay.

#### *Soil*

The soil in the experimental plots is typical of that found on farms in the locality of Amherst, Massachusetts. The alluvial soil, which according to Emerson (5) is at the bottom of the Hadley postglacial lake, is assumed to be a modified drift that accumulated at a late stage in the waning of the ice sheet. Beaumont (2, 3) has classified this glacial outwash material as Merrimac fine sandy loam. This material is 2 to 5 feet thick. Below is gravel that assures continual good drainage of the topsoil.

<sup>1</sup> Contribution No. 648 Massachusetts Agricultural Experiment Station.

### *Fertilizer*

The fertilizer was applied each year uniformly to all the experimental plots at the rate of 2,000 pounds per acre. It was a 5-8-7 commercial fertilizer typical of that used by farmers and commercial vegetable growers in this locality.

### *Tomatoes and cultural conditions*

The variety of tomatoes was a standardized Rutgers-Stokes strain. The seed was planted in flats in the greenhouse on April 10. Well-developed plants were set out in rows 4 feet apart each way in an open, unshaded field on May 28. Since the plants were allowed to develop on the ground when they were fully grown, the entire surface of the plots was covered with tomato vegetation. There was a variation among the different treatments, however, manure producing the greatest amount of vegetative growth, and Servall the least. The plants were not pruned at any time. A copper oxychloride sulfate spray, commonly called "C.O.C.S. spray," was applied three times during the growing season to prevent both early and late blight, but no late blight was observed even in unsprayed fields in the locality during 1947. The tomatoes were harvested August 25, 89 days after the plants were set out.

### *Mulches*

Provision was made for four groups of plots—three types of mulches and a control—with two replicates of each. Two of the mulches—horse manure and straw—were applied uniformly to the plots each of 6 years. The third mulch, banana fiber, was applied regularly for 3 years. At that time it became unobtainable, and Servall, shredded sugar cane stalks, replaced it for the last 3 years of the experiment. Since the horses were bedded with wood shavings, the horse manure consisted of horse feces, greatly diluted with wood fiber that carried some dried horse urine. The straw was from locally grown rye. Each spring after the plots were fitted, the different mulches were applied, in layers approximately 4 inches deep, over the entire surface as soon as possible after the newly set out tomato plants had become established. Each fall the mulches were plowed into the soil, thus adding organic matter to the mulch plots, but none to the check plots. The 4-inch layer of mulch tended to improve retention in the soil of moisture that came from rainfall. The mulches also prevented the growth of weeds and other plants and thus conserved all available plant food for the tomatoes.

### *Climatic conditions*

According to Sievers (7) and Stapleton (8), 6.82 inches of rain fell between May 28 and August 25, and there were 823 hours of bright sunshine. During the experimental period the temperature varied from 37° to 95°F. The least daily temperature range was 7°F. on June 8, and the greatest was 38°F. on June 23. The mean temperature was 64.6° for June, 73.2° for July, and 73.8°F. for August. The mean relative humidity was 68.5 per cent for June, 72.3 per cent for July, and 80.4 per cent for August.



*Collection and preparation of samples*

A sample of 12 tomatoes was collected for assay from each of the 12 plots. The tomatoes were selected with a great deal of care to assure fruits typical in size, conformation, uniformity of coloration, and degree of ripeness. The individual tomatoes of each sample were cut into quarters or smaller sections and disintegrated in a Waring Blender. When the tomatoes had been reduced to a homogeneous liquid, appropriate aliquots were removed for the various assays. Determinations were made for water, total solids, soluble solids, total sugars (invert), reduced ascorbic acid, carotene, calcium, magnesium, manganese, nitrogen, phosphorus, and potassium.

*Methods of assay*

All determinations, except those for carotene and soluble solids, were made by the official methods of the Association of Official Agricultural Chemists (1). The carotene content of the tomatoes was determined by the method employed by Holmes and Spelman (6) for squashes. The soluble solids were determined by converting, with the aid of Campbell's (4, p. 449) tables, the values for refractive index obtained with a Zeiss refractometer.

## RESULTS AND DISCUSSION

The detailed results obtained by the various assays are reported in table 1. The water content of the 12 samples of tomatoes was very similar, ranging from 92.6 per cent to 93.5 per cent. The averages for the individual plots varied from 92.7 per cent for the manure plots to 93.3 per cent for the check plots. The values obtained for the total solids were fairly uniform both within the groups and between the different groups. The range was from 6.5 per cent to 7.4 per cent, with averages for the different plots from 6.7 per cent to 7.3 per cent. The soluble solids varied from 6.00 per cent to 6.83 per cent. The lowest group average, 6.13 per cent, was for the check, and the highest, 6.61 per cent, was for the manure plots. The total sugars, considered as invert sugar, ranged from 2.7 per cent to 3.5 per cent, but the average values for the different plots were very similar. The reduced ascorbic acid in the different samples varied from 9 mgm. to 20 mgm. per 100 gm.; however, the average values were nearly identical for the four treatments. Tomatoes from the check plots contained the smallest average amount of carotene, 0.62 mgm. per 100 gm. The highest average value, 0.66 mgm., was obtained for the straw plots and for the Servall plots, which had the poorest coverage of foliage.

All the mulched plots produced tomatoes that contained more calcium than those of the check plot. The tomatoes that were richest in calcium, 25 mgm. per 100 gm., were grown on the Servall plots and the amount of calcium present in the straw-mulched and manure plots decreased in that order. The magnesium contents of the tomatoes grown on the mulched plots, 17, 20, and 19 mgm. per 100 gm., respectively, for the horse manure, straw, and Servall plots, were higher than that of the tomatoes from the check plots. Though the amount of man-

ganese in tomatoes from the manure plots was no larger than that in the tomatoes from the check plots, the straw-mulched and Servall plot tomatoes contained definitely larger amounts of manganese. The tomatoes from the manure and straw-mulched plots contained more nitrogen, 217 and 202 mgm. per 100 gm., respectively, than those from the check plots, but the lowest value, 148 mgm., was found in the tomatoes produced on the Servall plots. Each of the nine

TABLE 1  
*Effect of different mulches upon the composition of tomatoes*  
Results on fresh basis

SAMPLE*	WATER	TOTAL SOLIDS	SOLUBLE SOLIDS	TOTAL SUGARS (INVERT)	ASCORBIC ACID	CAROTENE	CALCIUM	MAGNESIUM	MANGANESE	NITROGEN	PHOSPHORUS	POTASSIUM
	per cent	per cent	per cent	per cent	mgm./100 gm.	mgm./100 gm.	mgm./100 gm.	mgm./100 gm.	p.p.m.	mgm./100 gm.	mgm./100 gm.	mgm./100 gm.
Check plots.....	93.3	6.7	6.00	3.0	9	.56	19	15	1.7	190	31	333
	93.2	6.8	6.26	3.2	12	.65	18	14	2.4	190	33	330
	93.3	6.7	6.13	2.9	17	.64	19	14	1.8	188	31	328
Average.....	93.3	6.7	6.13	3.0	13	.62	19	14	2.0	189	32	330
Manure plots.....	92.6	7.4	6.83	2.9	15	.70	18	16	2.1	225	37	364
	92.6	7.4	6.69	3.1	12	.61	16	15	2.1	216	39	366
	92.9	7.1	6.33	2.7	13	.57	28	19	1.7	210	38	364
Average.....	92.7	7.3	6.61	2.9	13	.63	21	17	2.0	217	38	365
Straw plots.....	92.8	7.2	6.39	2.9	12	.65	25	22	4.0	214	52	525
	93.5	6.6	....	3.0	14	.57	21	17	2.0	205	42	411
	93.2	6.8	6.19	2.7	12	.77	22	20	2.7	187	45	468
Average.....	93.2	6.8	6.29	2.9	13	.66	23	20	2.9	202	46	468
Servall plots.....	93.3	6.7	6.35	3.0	14	.74	23	19	2.7	171	44	460
	92.9	7.1	6.30	3.5	20	.67	24	18	2.0	137	48	443
	93.0	7.0	6.15	3.2	12	.56	28	19	2.6	135	50	473
Average.....	93.0	6.9	6.27	3.2	15	.66	25	19	2.4	148	47	457

\* Each sample comprised 12 selected tomatoes collected during the sixth year of the experiment.

samples from the mulched plots contained more phosphorus than any of the samples from the check plots. Though the potassium content of the tomatoes varied markedly for the different replicates, the average value, 330 mgm. per 100 gm., for the check plots was lower than any of the averages for the mulched plots.

Since the amounts of soluble solids and carotene were somewhat higher for the mulched tomatoes and the amounts of calcium, magnesium, phosphorus, and

potassium were definitely higher for mulched tomatoes than for those grown on the check plots, it would appear to be good cultural practice, particularly from the nutritional standpoint, to mulch tomatoes during their growing season. Horse manure and Servall are not universally available to tomato growers; thus rye straw would be the mulch of choice.

#### SUMMARY

An experiment of 6 years' duration was made to determine the possible effect of mulching upon the composition of tomatoes. A standardized Rutgers-Stokes strain of tomatoes was used. Plots with comparable soil were selected for three mulch treatments and a check, with two replicates of each. Four-inch layers of three types of mulch—horse manure with shavings, rye straw, and Servall (shredded sugar cane stalks)—were spread on the experimental plots as soon as the tomato plants were set out. In the last year, 12 samples of 12 mature tomatoes each were assayed for water, total and soluble solids, total sugars, reduced ascorbic acid, carotene, calcium, magnesium, manganese, nitrogen, phosphorus, and potassium. The water, total solids, total sugars, and ascorbic acid contents of the tomatoes were similar for the check and the mulched plots. The tomatoes from the mulched plots contained more soluble solids and carotene than those from the check plots. Larger amounts of calcium, magnesium, phosphorus, and potassium were found in mulch-plot tomatoes than in the control-plot tomatoes. Judged by the results noted above, mulching tomatoes increases the mineral, especially phosphorus and potassium, content of the tomatoes.

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# INFLUENCE OF SODIUM ON GROWTH AND COMPOSITION OF RANGER ALFALFA<sup>1</sup>

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Recently 10 samples of alfalfa that had been grown in Egypt were analyzed in this laboratory for their content of Na, which was found to vary between 0.08 and 0.86 per cent (table 1). This is in marked contrast to the Na content of New Jersey alfalfa. Bear and Prince (1) reported that the Na content of eight successive harvests of Atlantic alfalfa, grown in pots on 20 important New Jersey soils, was less than 0.05 per cent in all cases except one. The average Na content of 30 other miscellaneous samples of alfalfa from widely different soils in this state was found to be 0.05 per cent (14). Beeson (2) reports, however, that alfalfa has an average Na content of 0.43 per cent.

These differences in the Na content of alfalfa are undoubtedly related to the amounts of the element in the soils on which the plants were grown. Since the natural habitat of alfalfa is an alkaline-calcareous soil, it seemed logical to expect that this plant might absorb considerable amounts of Na if this was available and that possibly the element might play an important part in its mineral nutrition. Accordingly, it was decided to investigate this point.

It has been suggested (8, pp. 360-362) that Na may be beneficial to plants in one or all of the following ways:

- By replacing K in some of its functions when the supply of this nutrient is low.
- By preventing luxury consumption of K and thus conserving the supply of this element.
- By exerting an essential or beneficial effect regardless of the K supply.
- By overcoming any unbalance of the Ca-K ratio in the soil and in the plant.
- By increasing the absorption of other nutrient elements.

The first of these has received the most consideration, but it was decided to explore this possibility further with specific reference to the alfalfa plant. In preparation for outlining the method of attack it seemed advisable to set down the conditions that must be met if definite evidence was to be provided that Na can replace K in the functions within the plant. These were listed as follows:

1. Na must be absorbed by the plant.
2. Physiological functions in the plant must be normal in the presence of Na.
3. Growth of the plant must not be materially decreased when K concentrations are somewhat reduced and Na is substituted in part.
4. A range of Na concentrations must exist which would give growth increases in the presence of a low K supply. As a corollary, for complete replacement, the yield must equal that produced under an optimum K supply; for replacement in part, the yield must ap-

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proach or equal that under an optimum K supply; and, finally, for a beneficial effect of Na alone, the yield must exceed that produced under an optimum K supply.

5. For comparative purposes, the optimum K supply must be evaluated and comparisons made with Na under identical conditions.

6. Anion influences must be excluded.

It is believed that no definite conclusions can be drawn from a test of this type unless condition 5 has been determined beforehand. It should also be mentioned that an improvement or a beneficial result from Na may be obtained without meeting any or all of the previously listed conditions, but if it occurs it cannot be ascribed to a substitution of Na for K. In connection with this point, it has been shown that plants differ greatly in their capacity to absorb Na (3, 6, 14).

TABLE 1  
*Cation content of alfalfa grown in Egypt*  
In m.e. per 100 gm. dry matter

LOCATION	CUTTING NO.	SOIL TREATMENT	K	Na	Ca	Mg	CATION SUMMATION
Bilbeis.....	16	None	106	4	89	29	228
Khanka.....	8	None	43	38	119	27	227
Bilbeis.....	1	None	103	12	109	30	254
Suez.....	18	None	98	8	90	29	225
Kitaliya (Manfaloot).....	32	None	90	8	89	26	213
Zarkit el Dur (Manfaloot).....	17	None	74	4	127	26	231
El Mahras.....	8	Manure	39	37	94	24	194
Shaaraivi Pasha.....	8	None	63	21	110	26	220
Mallawi.....	15	Manure	76	4	94	22	196
Draw.....	2	None	87	13	85	21	206

If Na plays an important part in the nutrition of the alfalfa plant the lack of exchangeable Na in the soils of the humid eastern states may be one of the reasons why it is difficult to grow and maintain alfalfa stands for considerable periods in this area.

#### EXPERIMENTAL

Two experiments were designed, one in sand culture and the other in the field, to provide evidence on the influence of Na on the growth of alfalfa.

Ranger alfalfa plants were grown in sand culture through one harvest at different K levels, using the constant drip procedure of Robbins (12), to determine the optimum K level and to obtain plants which were characteristic of their K treatments prior to initiating the Na levels. Ten series of plants were used, five that included varying Na levels and five without Na. The composition of each of the nutrient solutions used is listed in table 2. Changes in K and Na were compensated for by varying the Mg. All other ions were held constant. The plants were grown on these solutions from April 30 to May 28.

At harvest time the plants were cut, leaves separated from stems, and green

and dry weights recorded for each portion of the harvest. The dry tissue was ground for analysis in a Wiley mill, and the K, Ca, Mg, and Na contents were determined by methods previously described (13, 14). Sulfur and P were also determined: S was precipitated as  $\text{BaSO}_4$  and weighed, and P was determined colorimetrically.

TABLE 2  
*K content and K-Na ratio of the nutrient solutions and K content of preliminary growth of alfalfa tops*

MOLES SALT PER LITER OF NUTRIENT SOLUTION							NUTRIENT SOLUTION COMPOSITION		K CONTENT OF PRELIMINARY GROWTH (DRY MATTER)
$\text{K}_2\text{SO}_4$	$\text{Ca}(\text{NO}_3)_2$	$\text{KH}_2\text{PO}_4$	$\text{Mg}(\text{H}_2\text{PO}_4)_2$	$\text{MgSO}_4$	$\text{Na}_2\text{SO}_4$	$\text{NaH}_2\text{PO}_4$	K Content	K-Na Ratio	
							p.p.m.		per cent
....	0.0035	0.00013	0.00044	0.004	....	....	5	....	0.69*
0.000063	0.0035	....	....	0.002	0.0019	0.001	5	0.027	0.69*
....	0.0035	0.00013	0.00044	0.004	....	....	5	....	1.33*
0.000063	0.0035	....	....	0.002	0.0019	0.001	5	0.027	1.33*
....	0.0035	0.001	....	0.004	....	....	39†	....	1.92
....	0.0035	0.001	....	0.002	0.002	....	39†	0.25	1.92
0.00075	0.0035	0.001	....	0.00325	....	....	97.5†	....	2.77
0.00075	0.0035	0.001	....	0.002	0.00125	....	97.5†	1.0	2.77
0.002	0.0035	0.001	....	0.002	....	....	195	....	3.37
0.002	0.0035	0.001	....	0.0015	0.00125	....	195	2.0	3.37

\* The difference in K content is because these plants received 19.5 p.p.m. K during the preliminary growth period.

† The K in these cultures was later reduced from 39 to 5 and from 97.5 to 37.5 p.p.m. K on May 15, 1947. Subsequent references to treatments will omit these changes.

The chlorophyll content of an aliquot of the fresh green tissue was determined by the method of Petering *et al.* (10).

The fertilizer treatments of the field experiment are listed in table 6.

#### DISCUSSION OF RESULTS

##### *Sand cultures*

At the time of harvest, on May 28, no buds had formed on any of the plants receiving 5 p.p.m. K without Na. The plants exhibited characteristic visual K-deficiency symptoms, and the leaves contained a low quantity of chlorophyll, as indicated by the data in table 3. Plants grown on all the other treatments were normal green in appearance, buds had formed, and blossoms were breaking. This indicates that normal growth processes were operating, even with the plants receiving Na.

The green and dry weights, leaf percentages, and the K and Na contents of the leaves, stems, and whole plants for all cultures are listed in tables 3 and 4.

With the different K levels, the yields increased progressively from the 5 to the 195 p.p.m. series, as might be expected. Data<sup>2</sup> have shown that yields of

TABLE 3  
*Effect of K content and K-Na ratios in nutrient solution on yield, leaf percentages, and chlorophyll content of alfalfa*

NUTRIENT SOLUTION COMPOSITION		YIELD			LEAF TO WHOLE PLANT	LEAF CHLOROPHYLL (DRY MATTER)
K Content	K-Na ratio	Green matter	Dry matter	Increase, dry matter		
p.p.m.		gm.	gm.	per cent	per cent	per cent
5	....	42.3	8.7	....	54.0	2.25
5	0.027	57.3	9.9	13.8	47.0	3.10
5*	....	48.7	9.1	....	58.5	2.54
5*	0.027	80.7	15.8	73.6	48.0	3.04
39	....	78.3	15.2	....	44.5	2.84
39	0.25	89.0	15.7	3.3	46.5	3.22
97.5	....	97.3	17.3	....	45.0	3.00
97.5	1.0	106.4	21.3	23.1	44.5	3.00
195.0	....	143.0	25.2	....	46.0	3.18
195.0	2.0	130.7	22.1	-11.5	47.0	3.50

\* Cultures through the first cutting received 19.5 p.p.m. K, which was later reduced to 5 p.p.m. K.

TABLE 4  
*K and Na content of leaves, stems, and tops of alfalfa and percentages of K and Na of tops in leaves*  
(Dry matter)

NUTRIENT SOLUTION COMPOSITION		K			Na			PERCENTAGE OF TOTAL IN LEAVES	
K content	K-Na ratio	Leaf	Stem	Tops	Leaf	Stem	Tops	K	Na
p.p.m.		per cent	per cent	per cent	per cent	per cent	per cent		
5	....	0.59	0.50	0.55	*	*	*	57.5	....
5	0.027	1.05	0.95	1.00	0.12	0.35	0.24	51.5	23.6
5†	....	0.81	0.82	0.81	....	....	....	57.5	....
5†	0.027	0.81	0.88	0.85	0.18	0.31	0.25	44.0	34.6
39	....	1.26	1.13	1.19	....	....	....	47.0	....
39	0.25	1.24	1.42	1.34	0.10	0.32	0.22	43.0	21.2
97.5	....	2.34	2.45	2.39	....	....	....	44.0	....
97.5	1.0	2.28	2.13	2.22	0.11	0.10	0.11	45.5	44.5
195	....	3.30	3.40	3.35	....	....	....	45.0	....
195	2.0	3.45	3.96	3.72	0.07	0.03	0.05	40.5	65.5

\* No Na could be detected in plants other than those growing in nutrient solutions to which it was added.

† See footnote table 3.

alfalfa are not appreciably increased with more than 195 p.p.m. K in solution culture.

<sup>2</sup> Unpublished.

To understand completely the influence of Na on the yields of alfalfa it is of importance first to consider the K content of the plants grown without Na. Table 4 presents these data. The significant fact to note is that the K contents of the plants in the first four series of treatments are below the established critical K content of alfalfa (1) and that in the fifth series the value nearly approaches it. If Na can replace K, it might be expected to occur when the K content is below the critical level. The data indicate that the plants are definitely in need of additional K.

The introduction of Na into these five series of cultures has resulted in increases in dry-matter yield in four of the series, as indicated by the data in table 3. The yield increases ranged from 3.3 to 73.6 per cent. They are not uniform, and they tend to vary considerably with the K-Na ratio in the culture solution. The greatest increase in yield was obtained from the culture that, prior to the second harvest, had received 19.5 p.p.m. K and that was later reduced to 5 p.p.m. K for the growth of the second cutting.

If Na has a direct effect upon the alfalfa plant, the expected result of the addition of Na to the substrate, when the K supply is high, would be an increase in yield. Since this did not occur, except in those cases when the K supply was inadequate, the logical inference is that Na replaced K. The fact that the largest yields of alfalfa were obtained from the highest K treatment containing no Na furnishes further evidence that the replacement effect is only partial. In this connection, Hoagland (5, pp. 166-167) has indicated that Na is absorbed too slowly to replace K effectively.

It is of interest to observe from the data in tables 3 and 4 that, in the low-K cultures the presence of Na exerts a marked influence on yields. In the light of this behavior, it is important to stress the fact that the presence of Na ions in culture solutions involving low-K levels must be avoided in plant physiological studies to isolate the influence of the K level. Mullison and Mullison (9) have shown that K-deficiency symptoms in barley appear earlier and are much more pronounced when Na is absent than when it is present.

The data in table 4 are concerned with the K and Na contents of the leaves, stems, and tops of the alfalfa plants grown in the various cultures. The proportions of the total K and Na in the tops that are present in the leaves are also listed. Plants of only three series of cultures, those with K-Na ratios of 0.027 and 0.25, contained more than 0.2 per cent Na in the stems or in the complete tops. The larger part of the Na in the plants of these three treatments was concentrated in the stems, only about 25 per cent being present in the leaves. Perhaps the most important point is that Na absorption by plants at the highest K level was small<sup>3</sup>. This was associated with no improvement of yields when Na was added. The previously suggested idea that Na can conserve K by preventing luxury consumption is obviously not confirmed by these results. In four of the five cultures, K absorption by alfalfa tops was increased<sup>3</sup> when Na was present in the substrate.

If analogies can be drawn between animal and plant systems, it may be possible to offer an explanation of the high concentration of absorbed Na in alfalfa stems

<sup>3</sup> When K content of Egyptian alfalfa was low, Na was high (table 1).

in comparison with the leaves. It is known that the K in animal blood is concentrated in the cells, whereas the Na is concentrated in the serum (4, pp. 427-428). In the alfalfa plant the Na may be present in the extracellular fluid, whereas the bulk of the K is present in the metabolizing cells. In animal blood the Na that is present in the serum aids in maintaining the proper osmotic effects. The Na in the extracellular fluid of alfalfa plants, in common with other similar ions, may perform a like function.

It was pointed out earlier (13) that K-deficient alfalfa plants are smaller and have higher leaf percentages than normal plants. The data in table 4 indicate that the leaf percentages of the plants supplied with Na were very similar to

TABLE 5

*Effect of cation content of nutrient solution on cation, P, and S contents of alfalfa tops and on ratios of Ca + Mg:K + Na*

NUTRIENT SOLUTION COMPOSITION		PERCENTAGE DISTRIBUTION OF CATION IN NUTRIENT SOLUTION AT START OF TEST				CATION CONTENTS* OF ALFALFA					P IN ALFALFA (DRY MATTER)	S IN ALFALFA (DRY MATTER)	Ca + Mg K + Na IN ALFALFA
K content	K-Na ratio	K	Na	Ca	Mg	K	Na	Ca	Mg	Summation			
<i>p.p.m.</i>											<i>per cent</i>	<i>per cent</i>	
5	....	0.8	....	43.8	55.4	15	....	97	37	149	0.86	0.37	8.9
5	0.027	0.8	30.4	43.8	25.0	26	10	77	33	146	0.76	0.37	3.1
5†	....	0.8	....	43.8	55.4	21	....	100	36	157	0.89	0.33	6.5
5†	0.027	0.8	30.4	43.8	25.0	22	11	74	33	140	0.59	0.31	3.1
39	....	6.2	....	43.8	50.0	30	....	73	34	137	0.63	0.27	2.8
39	0.25	6.2	25.0	43.8	25.0	35	10	75	31	151	0.53	0.29	2.4
97.5	....	15.6	....	43.8	40.6	62	....	72	26	160	0.58	0.27	1.6
97.5	1.0	15.6	15.6	43.8	25.0	57	5	68	19	149	0.51	0.27	1.4
195	....	31.2	....	43.8	25.0	87	....	58	20	165	0.52	0.24	0.9
195	2.0	28.6	14.3	40.0	17.1	96	2	65	16	179	0.56	0.24	0.8

\* In m.e. per 100 gm. dry matter.

† See footnote table 3.

those of plants supplied with high amounts of K without Na, again indicating that plant growth was normal in the presence of Na.

The equivalent-summation of K, Ca, and Mg per unit dry weight of alfalfa tissue is practically a constant over wide ranges of individual cations supplied in the nutrient solution or soil substrates. The cation-summation data, including Na, of the plants grown in this test are listed in table 5. To illustrate the relation between cation-equivalent values and ion concentration in the substrate, the proportions of the various cations present in the nutrient solution are likewise listed, as are also the P and S contents of the tissue.

These data indicate definitely that the addition of Na to the nutrient solutions did not upset the cation-constancy values of alfalfa but they did result in a slight depression of Ca and Mg absorption and in an increase in K absorption<sup>4</sup>.

<sup>4</sup> The extra K was not due to contamination in the Na cultures, for the K content of the salts used was checked and found to be negligible.



Richards (11) has reported that the value of Na when K is low is in reducing the antagonism between the divalent Ca and Mg and the monovalent K. The addition of Na to plants low in K in this experiment definitely improved the growth. This improvement may have been due to:

- The increase of K when Na was added.
- The functioning of Na in place of K.
- The decrease in the absorption of Ca plus Mg.
- A combination of any two or all three of the above factors.

If the main function of Na had been to reduce Ca and Mg absorption, this could still be a replacement of Na for K, since a dominant property of K is to reduce Ca and Mg absorption. Lucas and Scarseth have suggested (7) that the ratio of Ca + Mg:K for alfalfa should be less than 3.5 to avoid K deficiency. The ratios of Ca + Mg:K + Na in table 5 show that all plants receiving Na, including the low-K plants, had ratios of divalent:monovalent cations that were less than 3.5.

The increased absorption of K by plants grown in solution cultures in the presence of Na is of considerable interest, since other investigators have observed this similar behavior by plants grown in soils and have ascribed it to an increase in availability of soil K. The data of these tests show, however, that it occurred also in solution culture.

A possible factor, not studied, is that the increased K content of the plant tops may be due to a replacement of K in the roots by Na with its subsequent movement to the tops. It is believed that this point cannot be ignored, especially since it has been shown that a great difference exists in the Na content of leaves and stems. Recognition of this fact leads to a possible inference that yield increases of alfalfa in these tests where Na has been added may be due in part to an increase in K content due to the root replacement of K, rather than to the direct influence of Na.

When the K content of the culture solutions was greatly reduced, the increase in absorption of Ca and Mg by the alfalfa plant was greater than that of Na. This behavior suggests that Ca and Mg ions are more mobile than Na in the alfalfa plant. If this is so, it may be necessary to reduce the concentrations of Ca or Mg or both in the nutrient solution to increase Na absorption.

The slightly greater cation-equivalent value of the tissue produced on the solution with a K-Na ratio of 2.0 was probably due to the slightly greater osmotic pressure of this culture solution in comparison with the others. It was necessary to increase the osmotic pressure in order not to unbalance greatly the ratio of divalent to monovalent cations when using large quantities of both K and Na in the solution. It is quite possible that the slightly lower yields from this culture when Na was added may have been the result of a deficiency of Mg, even though visual symptoms were not apparent on the plants.

In the K series, both the P and S contents increased as the K content in the plant tissue decreased. This had been observed in earlier studies with K and

alfalfa<sup>5</sup>. The addition of Na to low-K plants resulted in a decrease in P. This decrease was toward the normal and may have helped to improve the physiological condition of K-deficient plants. Excess P is also a factor influencing abnormal Fe utilization (15). The S contents, however, were unaffected by Na.

Na did not appear to have an essential role in the nutrition of Ranger alfalfa, but the results indicate that the study of Na is of tremendous importance because of the influence of this element on the absorption and utilization of the elements that are considered to be essential.

*Field tests of response of Ranger alfalfa to Na applications*

NaCl was added to Ranger alfalfa plots at the rate of 30 pounds Na per acre. In each pair of plots equivalent amounts of K or Na were used to eliminate the anion effect of Cl. The yields of alfalfa and the K and Na contents are recorded in table 6.

TABLE 6  
*Effect of fertilizer treatments on yield and K and Na contents of second and third cuttings of field-grown alfalfa*  
(Dry matter)

TREATMENT*	SECOND CUTTING			THIRD CUTTING		
	Yield	K	Na	Yield	K	Na
	lbs.	per cent	per cent	lbs.	per cent	per cent
K, P, B. ....	3,240	1.32	0.02	1,560	1.25	0.02
K, P, B, Na. ....	3,220	1.28	0.08	1,630	1.67	0.05
K, P, B, N. ....	3,600	1.06	0.02	1,540	1.19	0.02
K, P, B, N, Na. ....	3,540	1.09	0.06	1,600	1.03	0.06

\* All fertilizers were applied immediately after first cutting. N, P, K was applied at the rate of 60 pounds N,  $P_2O_5$ , and  $K_2O$  per acre respectively; B, at 20 pounds of borax per acre, and Na, as NaCl, in amounts equivalent to K.

It was shown previously in this paper that increases in dry-matter yields were obtained when Na was added to culture solutions containing small amounts of K. Previous data on the K content of alfalfa grown on these plots had indicated that K was near the critical limit, and it was believed that Na applications might result in increased yields. The data in table 6, however, indicate no significant yield response to Na applications even though the Na content of the tissue from the Na plots was slightly increased.

The available-K content of the soil was not low enough to approach the concentration of K employed in the low-K nutrient solutions, the plants in which showed a response to Na applications. Whether or not the low K concentration at which Na applications show a beneficial effect can be approached in the soil is highly problematical. This investigation will be continued for several years.

<sup>5</sup> Unpublished data.

## SUMMARY AND CONCLUSIONS

A preliminary study was made of the influence of Na on the growth of Ranger alfalfa under a particular set of conditions in sand culture and in the field.

The study in sand culture resulted in the following conclusions:

Na was utilized by alfalfa plants, with resulting increase in yield, particularly when the K supply was low. This is explained tentatively as due to a partial replacement of K by Na.

Physiological processes appeared to be normal in the presence of Na.

Most of the absorbed Na was present in the stems, suggesting a replacement of K by Na rather than an important physiological function of Na alone.

Na did not retard luxury consumption of K.

Plants exhibited the usual cation-equivalent constancy when Na was present in the nutrient solution.

The addition of Na to low-K plants usually resulted in an increase in the K content and a decrease in Ca and Mg.

Plants that received large amounts of K absorbed only slight amounts of Na.

It is possible that the absorption of Na might have been increased if Ca and Mg concentrations in the nutrient substrate had been reduced.

The S content of alfalfa was not influenced by Na.

P absorption was decreased in the presence of Na, especially in those cases where K-deficiency symptoms were noted.

The influence of Na on the absorption and utilization of the essential elements may be more significant than its ability to replace K.

The field study led to the following conclusion:

Na did not improve alfalfa yields in the field when the K content of alfalfa tissue was near the critical limit.

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## SOIL DENSITY AND ROOT PENETRATION

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In a previous paper (4) we described two subsoils that exhibited peculiar water-holding properties. In general, these subsoils showed only a slight decrease in moisture content during the growing season. This decrease was attributed to slow drainage. Samples of these subsoils were compacted in the laboratory to about the density that occurred in the field to ascertain whether sunflower roots would penetrate them. From these preliminary experiments, it was found that, in one case at least, sunflower roots were unable to penetrate the compacted sample when the apparent specific gravity was 1.8 or above.

The experiments reported in this paper were carried out with a number of soils of widely different water-holding characteristics to determine, if possible, the threshold density, above which sunflower roots were unable to penetrate. The soils used ranged from fairly coarse sands to typical clay adobes.

### EXPERIMENTAL PROCEDURE

A number 2 friction-top can was calibrated so that the volume of a 500-gm. sample of soil could be obtained fairly accurately by measuring the average distance from the top rim of the can to the surface of the soil, which was as nearly level as possible. By packing the soil to a given distance below the rim, samples of the desired densities within fairly close limits were obtained. Samples of each soil were moistened with a spray of water from an atomizer, the soil being stirred while the water was being applied. The sample was weighed from time to time as the water was being applied to make certain that too much water was not added. The amount of water added in each case was less than the amount needed to saturate the soil at the desired density, and it varied somewhat with each sample, according to the judgment of the operator. The sample was then tamped into the can, a little at a time, until compacted to a predetermined volume. In the high-moisture samples, each layer was tamped until it glistened slightly, indicating a small quantity of water on the surface. The samples of low-moisture content were packed layer by layer, according to the judgment of the operator. After a little practice, it was possible to pack the entire sample to about the desired volume. No claim is made for uniformity of compaction in the whole mass, and the different layers probably varied slightly in density.

Several small errors are involved in the measurements from which the specific gravity calculations were made. Sometimes, the packing of the soil caused the bottom of the can to bulge, thus changing the volume slightly. In other cases, small quantities of soil were lost in the process of spraying or in cleaning the pan in which the mixing was done. These errors may help to account for differences in the beginning and final values of the moisture contents and specific gravities.



In other cases, it was impossible to make final specific gravity determinations because of the crumbly condition of the soil.

When the tamping was completed, the surface of the soil was covered with a thin layer of wax, consisting of 80 per cent paraffin and 20 per cent petrolatum, so that soil above the seal could be watered at intervals without changing the moisture content below the wax. From 120 to 220 gm. of loose soil was placed on the wax seal, watered, and planted with sunflower seeds. Experience has shown that sunflower roots grow through this wax readily. The sunflower plants were grown until they were 4 to 6 inches tall and had six to eight leaves. Then the cans were cut in half longitudinally with a hack saw, and samples of soil were taken for moisture and specific gravity determinations.

#### SOILS

Meyer clay adobe is described as a dark brown to nearly black clay, of pronounced adobe structure, from 4 to 6 feet deep. The soil structure and texture appear to be fairly uniform down to the parent material just above the rock, which is shale. It is probably residual in origin. The apparent specific gravities in the top 3 feet are reported to vary from 1.48 to 1.57.

Delano loamy sand is a moderately weathered secondary soil having a calcareous subsoil. It is derived mainly from acid igneous rock.

Fresno sandy loam is classed as a medium textured, maturely weathered secondary soil with calcareous hardpan, derived from acid igneous rock.

Holland sandy loam is a medium textured primary soil developed on bedrock. At a depth of 18 to 48 inches decomposed granitic bedrock, partly weathered, is usually present. The soil is noncalcareous and ordinarily contains quartz particles and mica.

Aiken clay loam is also a primary soil developed on bedrock from basic igneous rock. It is a friable, granular clay loam and exhibits some interesting water-holding characteristics. It is derived from volcanic rocks of low quartz content and is noncalcareous, but contains some iron concentrations or shotlike pellets.

Bale gravelly loam is a secondary soil derived from rhyolitic rock and contains a considerable amount of gravel. The upper subsoil layer is moderately compact and increases in density with depth. Samples at a depth of 4 or 5 feet have shown apparent specific gravity values as high as 1.88. The dense subsoil, however, is not classed as hardpan.

Dublin clay adobe is a dark gray to black secondary soil derived from sedimentary materials. It has a typical adobe structure, and the soil in the area from which the samples were taken showed increasing density with depth.

Chualar loam is a dark dull brown, coarse textured, gritty loam derived from the weathering of old valley-filling deposits made up of granitic or quartz-bearing rocks. It is a moderately mature soil underlain by a compact subsoil.

Yolo clay loam is a dark brown recent alluvial soil derived from mixed sedimentary rocks.

The mechanical analyses of the soils used are given in table 1.

## RESULTS

The real specific gravities of the soils, which varied from 2.58 to 2.66, were used in computing the pore space. The average soil-moisture contents of the

TABLE 1  
*Mechanical analyses of soils\**

SOIL	CLAY (0.005 mm.)	SILT (0.05-0.005 mm.)	SAND (1.0-0.05 mm.)
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
Aiken clay loam.....	49	26	25
Bale gravelly loam.....	39	31	30
Chualar loam.....	10	18	72
Delano loamy sand.....	11	17	72
Dublin clay adobe.....	37	36	27
Fresno sandy loam.....	12	29	59
Holland sandy loam.....	18	19	63
Meyer clay adobe.....	38	26	36
Yolo clay loam.....	44	42	14

\* By the hydrometer method of Bouyoucos.

TABLE 2  
*High soil density as a deterrent to penetration by sunflower roots*

SOIL	PORE SPACE SATU- RATION* AT INDICATED DENSITY	AVERAGE MOISTURE CONTENT	AVERAGE DENSITY OF COMPACTED SOIL†
	<i>per cent</i>	<i>per cent</i>	
Aiken clay loam.....	30.03	22.81	1.46
Bale gravelly loam.....	17.96	16.83	1.80
Bale gravelly loam.....	19.88	19.11	1.74
Chualar loam.....	12.82	8.81	1.95
Delano loamy sand.....	10.37	7.64	2.06
Dublin clay adobe.....	22.59	20.93	1.63
Fresno sandy loam.....	15.89	11.65	1.86
Holland sandy loam.....	16.03	14.07	1.86
Holland sandy loam.....	19.74	14.11	1.74
Meyer clay adobe.....	18.51	16.89	1.76
Meyer clay adobe.....	27.48	22.88	1.52
Yolo clay loam.....	21.05	20.22	1.68
Yolo clay loam.....	27.77	23.47	1.51

\* Amount of water needed to saturate the soil, expressed as percentage of dry weight.

† No roots penetrated any of the compacted soils.

compacted soils at the end of the experiment are given in table 2. It will be noted that the moisture contents are less than the theoretical percentages of moisture necessary to saturate the soils completely. There was little or no moisture extraction from the compacted layer during the course of the experiment. This lack of extraction of moisture indicates the absence of roots in the compacted

soil. Visual examination of the samples for roots, after the cans were cut, substantiated these findings. The average densities in the last column of the table were obtained by coating suitable samples of the compacted soil with a thin layer of paraffin and calculating the values from the weights of the sample in air and in water, making a correction for the paraffin. The densities obtained with the sandy soils seemed to be a little higher than those possible to obtain from the clays by the same compacting methods. It was impossible to obtain high densities with Aiken clay loam and Dublin clay adobe by using the same method that gave high densities with some of the sands.

Table 3 gives a comparison of densities obtained by mechanically compacting and by settling soils with water, and the resulting moisture contents after sun-

TABLE 3  
*Soil densities obtained by compacting and by settling with water*

SOIL	MOISTURE EQUIVALENT	PERMANENT WILTING PERCENTAGE	AVERAGE CALCULATED MOISTURE AT START OF EXPERIMENT	AVERAGE MOISTURE AT END OF EXPERIMENT	AVERAGE DENSITY
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	
Aiken clay loam.....	29.1	22.36	23.39	22.81	1.46
Aiken clay loam.....	29.1	22.36	saturated	22.10	1.06*
Bale gravelly loam.....	21.0	10.76	15.71	16.83	1.80
Bale gravelly loam.....	21.0	10.76	saturated	11.85	1.49*
Delano loamy sand.....	8.1	4.37	8.25	7.64	2.06
Delano loamy sand.....	8.1	4.37	11.58	4.29	1.56*
Fresno sandy loam.....	9.4	3.59	11.85	11.65	1.86
Fresno sandy loam.....	9.4	3.59	12.35	3.16	1.46*
Holland sandy loam.....	14.0	10.20	12.31	14.07	1.86
Holland sandy loam.....	14.0	10.20	14.09	9.53	1.44*
Meyer clay adobe.....	32.0	18.60	16.15	16.89	1.76
Meyer clay adobe.....	32.0	18.60	saturated	19.63	1.48*

\* Settled with water. Roots penetrated these soils but not the other member of each pair.

flower roots had had an opportunity to enter the packed or settled soils. The data on the compacted soils are taken from table 2. Two sets of results are presented for each soil. The first soil of each pair was compacted to a high density mechanically, whereas the second was settled with water. Of the soils settled by water, some were wetted to field capacity and others were saturated. The saturated soils were allowed to stand overnight, after which the excess moisture on the surface was drawn off with a pipette. These samples were then placed in an oven at 105°C. for several hours until the surface was dry enough to receive the wax covering. The drying, however, was not continued long enough to reduce appreciably the moisture content within the soil mass. Except at the surface, the soil was saturated. The heating probably drove out most of the air of the water in the soil.

The moisture equivalents and permanent wilting percentages were obtained

in the usual way on soil that had been fragmented during collection. These values are meaningless so far as the samples of high density are concerned, as pointed out in a previous publication(4). At the end of the experiment, it was found that those samples that had been settled with water had been entered by roots and that the soil moisture was reduced to about the permanent wilting percentage. The densities obtained by settling the soil with water were lower than those obtained by mechanical packing.

Table 4 gives the results of trials with some of the soils that were compacted at relatively low moisture contents. The results indicate that it is possible to obtain relatively high densities by compacting soils at fairly low moisture contents. This is in agreement with the results reported by Parker and Jenny (3). Though no roots were found in the compacted soils at these low moisture contents, it was impossible to tell whether the absence of roots was due to the compaction or to the

TABLE 4  
*Dryness and compaction of soils as deterrents to penetration by sunflower roots*

SOIL	MOISTURE EQUIVALENT	PERMANENT WILTING PERCENTAGE	AVERAGE SOIL-MOISTURE CONTENT	AVERAGE DENSITY*
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	
Aiken clay loam.....	29.1	22.36	13.54	1.22
Chualar loam.....	6.3	3.65	4.14	1.99
Delano loamy sand.....	8.1	4.37	4.36	1.80
Dublin clay adobe.....	26.0	15.36	13.33	1.54
Meyer clay adobe.....	32.0	18.60	12.01	1.51
Yolo clay loam.....	26.4	15.28	9.94	1.45

\* No roots penetrated any of these soils.

dry condition of the soil. The failure of sunflower roots to penetrate loose soils at moisture contents below the permanent wilting percentage substantiates previous work (1).

#### DISCUSSION OF RESULTS

Substantiating work previously reported (4), the results presented in this paper indicate that certain soils, when compacted to relatively high densities, do not permit entrance of roots of sunflower plants. Field experiments also show evidence of lack of penetration by roots where high densities occur naturally. Thus far, pine trees, grape vines, fig trees, and chaparral have shown little or no extraction of moisture from subsoils of about the same high densities reported in this paper. In other words, plants on soils having dense subsoils may be as shallow-rooted as those on typical hardpan soil.

Among the sandy soils, particularly those which seemed gritty and contained a considerable amount of angular material, it was possible to obtain densities of about 1.9 or above. It was impossible to obtain as high densities with some of the clay soils as with the sands.

The soil density above which roots do not penetrate is not necessarily the same

for all soils. No roots were found at densities of 1.9 or above. In several cases when the density was 1.7 or 1.8, there was likewise no root penetration. On the other hand, there was no penetration into the clay soils when the density reached values of 1.6 or 1.7. The lowest density (1.46) into which roots failed to penetrate was obtained with Aiken clay loam.

The amount of water added to each sample during stirring was less than the amount that would saturate the soil at the desired density. In a few cases where this amount was exceeded accidentally, the desired density could not be obtained, and the sample had to be discarded. In most cases the soil, when ready for packing, appeared to be in a condition that would be about right for tillage operations in the field. The fact that high densities were obtained with soils of about this moisture content indicates how easily a plow sole may be started. At the other extreme, the success in obtaining fairly high densities with some of the soils at relatively low moisture contents seems to point to the fact that plow soles may also be formed by working soils when the moisture content is fairly low.

Field experience with compact subsoils shows that drainage is slow, the moisture contents of the soil at the 4- or 5-foot depths sometimes decreasing only 2 or 3 per cent during the growing season, even where no water was applied. The slow decrease in moisture content at these low depths was probably due to drainage, and not to extraction of moisture by plant roots. Sometimes the soil was found saturated at these depths during the summer months.

Table 3 shows that soil densities obtained by settling with water are considerably lower than those obtained by mechanically compacting the soil at suitable moisture contents. Sunflower roots penetrated the soils settled by water but not those mechanically compacted to high densities. That the failure of roots to penetrate the compacted soils may have been due to small size of pores rather than to lack of oxygen is indicated by the fact that roots penetrated the saturated noncompacted soils from which most of the air had been expelled by heating.

The moisture contents of the densely packed soils were about the same when the cans were opened as they were when first packed. Furthermore, the clays, which were fairly high in colloids, showed no tendency to crack.

The threshold densities above which sunflower roots did not enter seemed to be about 1.75 for the sands and varied from about 1.46 to 1.63 for the clays.

It should be pointed out that some sandy soils, which are generally considered easy to work, may readily be compacted at a depth varying with the type and weight of the tillage implement used. These plow soles, however, are probably not dense enough to cause serious trouble in most cases, but may decrease the rate of penetration of water. Furthermore, they are apparently not compact enough to prevent entrance by plant roots.

With subsoils dense enough to prevent entrance of roots, the moisture equivalent and permanent wilting percentage are essentially without meaning, because in the ordinary procedure of determining these values with fragmented samples, the density of the soil is changed in taking the sample from the field, and the soil is not again compacted to its original density. The same objections may be raised against other means of attempting to determine soil-moisture relations of



compacted soils, particularly when the structure of the soil is disturbed and cannot be brought back to its original condition. The permanent wilting percentage as determined in the field (2) is simply the permanent wilting percentage of the soil as deep as the roots are able to penetrate. Fluctuations in moisture content below the depth of root penetration are due to deep penetration of rain or irrigation water, to variations in the water table, and to drainage; most of these are probably small in both relative and absolute amounts. In field experiments where dense subsoils are present, it is probably futile to continue sampling below the depth of rooting, because changes in moisture content may be due to drainage rather than to extraction of moisture by roots.

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# RELATIONSHIP OF PLANT DEVELOPMENT TO THE CAPACITY TO UTILIZE POTASSIUM IN ORTHOCLASE FELDSPAR<sup>1</sup>

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Mineral soils, with few exceptions, contain larger quantities of potassium than of any other major element considered necessary for plant growth. Most of this potassium is in the insoluble form. Many investigators have noted that certain plants have greater capacity than others to utilize the insoluble potassium in the feldspars, although there is not always agreement as to which plants have the greater capacity. The authors have found no record in which the degree of evolution of plants was considered in relation to their capacity to utilize the insoluble potassium. This experiment was performed in an attempt to learn whether any such relationship exists.

It has undoubtedly been noted that many of the early forms of plants such as the mosses and the lichens have to a great extent the capacity to obtain the ions necessary to their maintenance under environmental conditions in which highly developed plants could not survive. Wolff's old analyses (6) indicate that these plant forms of early origin use but little of such elements as calcium and nitrogen. In most of them, the elements which predominate are not the characteristic nutrient elements of seed plants.

The capacity of plants of the lower orders to obtain ions from rocks and from dust blown upon them is characteristic of plants not easily used for laboratory experiment because of their slow development. For this reason, this experiment was performed with members of the seed plant kingdom. The plants chosen represented families in the ascending order of their evolution as nearly as such evolutionary gradation could be made.

## MATERIALS AND METHODS

In choosing the species, the plan of classification of such authorities on plant anatomy as Pool, (5) was followed. It is not conclusive that physiological behavior follows an anatomical pattern. Mez (3) has classified plant development from a serological point of view. The degrees of development as indicated by him do not vary greatly from those based on plant structures. Regardless of minor differences in gradation, however, it is known that such plants as the Compositae, Labiatae, Scrophulariaceae, Campanulaceae, and Boraginaceae, as a group, are extremely well developed. It is known that such plants as the Ra-

<sup>1</sup> Contribution No. 663, department of agronomy, Massachusetts Agricultural Experiment Station, Amherst, Massachusetts. The data in this paper are taken from a thesis submitted by the senior author to the University of Massachusetts graduate school in partial fulfillment of the requirements for the degree of doctor of philosophy. The junior author is research professor of agronomy.

nunculaceae, Magnoliaceae, and even the economically rather important families, such as the Cruciferae, Leguminosae, and Rosaceae, are low in the seed kingdom.

In this experiment a plant of the Ranunculaceae represented the lowest order used. A member of the Compositae was chosen as the most highly developed plant. Between these two extremes were chosen members of the families listed in table 1 in the approximate order of their development.

This investigation was carried out in the greenhouse over a period of approximately one year, but not all plants were grown at the same time.

TABLE 1  
*Classification of experimental plants*

COMMON NAME	ORDER	FAMILY	SPECIES
Larkspur	Ranales	Ranunculaceae	<i>Delphinium</i> sp.
Rape	Papaverales	Cruciferae	<i>Brassica Napus</i>
Poppy	Papaverales	Papaveraceae	<i>Papaver somniferum</i>
Lespedeza	Rosales	Leguminosae	<i>Lespedeza Stuei</i>
Velvet leaf	Malvales	Malvaceae	<i>Abutilon Avicennae</i>
Geranium	Geraniales	Geraniaceae	<i>Geranium maculatum</i>
Pinks	Caryophyllales	Caryophyllaceae	<i>Dianthus barbatus</i>
Primrose	Primulales	Primulaceae	<i>Primula vulgaris</i>
Onion	Liliales	Liliaceae	<i>Allium Cepa</i>
Parsley	Umbellales	Umbelliferae	<i>Petroselinum hortense</i>
Squash	Cucurbitales	Cucurbitaceae	<i>Cucurbita maxima</i>
Tomato	Polemoniales	Solanaceae	<i>Lycopersicon esculentum</i>
Phlox	Polemoniales	Polemoniaceae	<i>Phlox Drummondii</i>
Heliotrope	Polemoniales	Boraginaceae	<i>Heliotropium peruvianum</i>
Snapdragon	Personales	Scrophulariaceae	<i>Antirrhinum majus</i>
Rye	Graminales	Gramineae	<i>Secale cereale</i>
Bluebell	Campanales	Campanulaceae	<i>Campanula rotundifolia</i>
Buckwheat	Polygonales	Polygonaceae	<i>Fagopyrum esculentum</i>
Spinach	Chenopodiales	Chenopodiaceae	<i>Spinacia oleracea</i>
Scarlet sage	Lamiales	Labiatae	<i>Salvia splendens</i>
Sunflower	Campanales	Compositae	<i>Helianthus</i> spp.
Lettuce	Campanales	Compositae	<i>Lactuca sativa</i>

One hundred and thirty-two glazed porcelain crocks of 1-gallon capacity were used. These were thoroughly cleaned and dried before soil was added. Each crock was supplied with glass tubing, 1-inch in diameter, for addition of water and water-soluble nutrients.

The soil used was Merrimac sandy loam, a glacial outwash type, taken from the University of Massachusetts experimental plots. No potassium had been added to it in the last 55 years. Lime had been added at the annual rate of  $\frac{1}{2}$  ton per acre for the last 10 years. The soil was brought into the greenhouse, allowed to air-dry for several days, and then screened. Eight pounds of this screened, air-dried soil was supplied to each crock.

To one series of crocks, used for controls, no potassium was added; to another, soluble potassium in the form of potassium chloride at the rate of 287 pounds per

acre; and to the third series, orthoclase feldspar (6.5 per cent  $K_2O$  by analysis) at a rate equal in  $K_2O$  to that which was added to the potassium chloride series. All treatments were made in duplicate.

To all three of the series was added nitrogen in the form of ammonium nitrate at the rate of 214 pounds of nitrogen to the acre, and monocalcium phosphate at the rate of 611 pounds per acre.

These nutrients were maintained constant throughout the investigation because, as suggested by Wolff (6), the composition of the ash of plants can be changed by varying the salts in the nutrient medium.

On the basis of Petrie's (4) report, in which he indicated that the ionic state and high mobility of potassium make possible an actual loss from the tissue to the soil after maturity, the plants grown in this experiment were not allowed to pass maturity. The part of the plant above ground was harvested, dried at  $60^{\circ}C$ . for 48 hours, then ground. A representative sample was taken for analysis.

Analysis was by the A.O.A.C. method for plants (1, pp. 121-122, analyses 12-16, 12-17, and 12-19.)

#### RESULTS AND DISCUSSION

Table 2 shows the results of the chemical analyses. From the data it is evident that plants in the lower stages of evolution utilize considerably more potassium from both soluble and insoluble sources than do plants in the higher stages of development. This holds true for plant orders studied in both monocotyledonous and dicotyledonous groups. The fact that fewer representatives of the monocotyledonous plants than of the dicotyledonous were studied should be noted in making deductions from this work. There is evidence that the dicotyledonous plants are more ancient than the monocotyledonous plants.

The degree of efficiency of the lower order of seed plants as compared to the higher orders in obtaining potassium may be observed from the first five plants of the lowest orders—larkspur, rape, poppy, lespedeza, velvet leaf. Here the average percentage gain of plants grown with orthoclase feldspar over the control plants is 75.4 per cent. In contrast to this, the average percentage gain of the five most highly developed plants—buckwheat, spinach, scarlet sage, sunflower, lettuce—is 7.6 per cent. Thus the percentage gain of the five lowest plants is about ten times that of the five highest.

The average percentage gain of the first half of the plants listed over the last half is 2.8. In other words, the average capacity of the first half or lower plants is more than twice as great as that of the last half or higher species used.

There are, however, some conspicuous exceptions to the trend indicated in this generalization. The tomato, the snapdragon, and the rye show percentage gains higher than their degree of development would indicate (table 2). The tomato seems especially worth noting. Its behavior here approximates more nearly the lower plants than the high. In a magnesium-deficiency experiment it was found (2) the entire Solanaceae family, though of the higher order of seed plants, showed decided deficiency symptoms just as did the lower order of seed plants. This may be a coincidence, but the Solanaceae in both experiments were exceptions in



their behavior. The Solanaceae are quite high in the order of development but physiologically behave as low seed plants.

It was observed during the experiment that squash, larkspur, tomato, phlox, and poppy plants made similar amounts of total growth in soils receiving insoluble potassium and in those receiving soluble potassium, but there was a marked difference in the color of the plants. The soluble treatment produced dark green plants; the insoluble treatment produced plants of a lighter green.

TABLE 2

*Percentage of potassium in oven-dried plant material, and percentage gain due to added potassium compounds*

Plants arranged from low to high order of development

PLANTS	POTASSIUM IN PLANTS			GAIN IN POTASSIUM		
	Controls (no K added)	Insoluble K (feldspar)	Soluble K (KCl)	Insoluble K over controls	Soluble K over controls	Soluble K over insoluble
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
Larkspur.....	0.19	0.51	0.58	169	205	14
Rape.....	1.06	1.78	2.69	68	154	15
Poppy.....	1.10	1.78	2.72	62	147	53
Lespedeza.....	0.47	0.74	0.98	57	108	32
Velvet leaf.....	1.42	1.72	2.46	21	73	43
Geranium.....	0.55	0.85	1.17	55	113	38
Pinks.....	1.38	1.67	2.15	21	56	28
Primrose.....	0.47	0.61	0.87	30	85	43
Onion.....	4.36	4.88	5.10	12	17	4
Parsley.....	1.46	1.61	3.11	10	113	93
Squash.....	1.12	1.26	1.48	12	32	17
Tomato.....	0.65	0.88	0.99	35	52	12
Phlox.....	1.07	1.25	1.51	17	41	21
Heliotrope.....	2.31	2.55	2.82	10	22	10
Snapdragon.....	0.53	0.70	0.86	32	62	22
Rye.....	0.76	1.00	1.16	32	53	16
Bluebells.....	0.92	1.06	1.23	15	34	16
Buckwheat.....	1.41	1.47	2.14	4	52	46
Spinach.....	1.42	1.47	2.56	3	80	74
Scarlet sage.....	0.74	0.85	1.13	15	52	33
Sunflower.....	0.58	0.64	1.17	10	100	83
Lettuce.....	1.04	1.11	1.50	6	44	35

Deficiency symptoms were not pronounced in all cases. The intake of potassium ion from feldspar may exert some effect on the physiological balance of the plant. Further investigation along this line may prove very valuable.

It was observed that most of the plants of the lower orders grown in the control medium showed potassium deficiency earlier than did those of the higher orders. Lespedeza, pinks, velvet leaf, larkspur, geranium, and rape showed deficiency early. Deficiency symptoms were not evident, however, in the poppy, which is also one of the low seed plants. This is probably due to the character-

istic leaf blade, which, being much indented, makes difficult detection of less pronounced symptoms. Of the higher plants, rye and scarlet sage showed deficiency. Those in the intermediate stages of development which showed the deficiency were primrose and heliotrope. It is within reason to assume that selection and domestication have changed these plants in some way.

It seems rational to inquire why the low order plants have so much greater capacity to extract the potassium ion from minerals classified as relatively insoluble. It is entirely plausible to assume that the soil in the early periods of the earth's history was not the weathered soil of today. New soils do not readily yield their elemental constituents to plant life as do old soils. Consequently it was imperative in those periods that for their survival, plants develop the capacity to seize ions from soils less weathered from the matrix rock.

The lower nonseed plants of the early geological periods had then and now a greater capacity to use the so-called "unavailable" ions. It would seem evident from this experiment that the lower seed plants have this capacity also, though in a diminishing degree.

Although the efficiency in obtaining the necessary ions for maintenance of life was and is greater in the older plants than in the newer seed plants, the quantity of ions such as the alkali and alkaline earth elements was less in the nonseed plants than in the seed plants. This has long been observed. It is well known that ashes of hardwoods are better for fertilizer than ashes of conifers and softwoods. The conifers are old plants, and the intake of potassium, sodium, calcium, and magnesium is low. Even though ions have leached out from what are now coal measures, the ashes indicate that the very old plants from which the coal was formed contained predominantly salts of weak acids and weak bases.

The fact that the older seed plants are more efficient than the newer ones in obtaining their ions from what might be called "unavailable" sources, indicates that their direct ancestors lived in an environment where frugality and slow growth were a necessity.

Although a limited number of plant families was used in this experiment, it is reasonable to assume that some economic plants would be more efficient than others in extracting their potassium from feldspar. Such lowly seed plants as cotton, okra, apples, peaches, berries, roses, alfalfa, clovers, locusts, poppy, cabbage, cauliflower, and radishes should be expected to obtain their potassium from insoluble compounds more readily than the more highly developed plants such as asters, sunflowers, grasses, and mints.

#### SUMMARY

Twenty-two seed plants of varying degrees of development were grown in soil in three series. To one series no potassium was added; to another, potassium chloride; to the third, feldspar in quantity equivalent in potassium content to the second series. At maturity the potassium content of the plants was determined by chemical analysis, and percentage gains in all series were computed.

Statistically the percentage gain of potassium from both soluble and insoluble

sources tended to decrease as the plants ascend from the lower to the higher order of development.

In the control medium, plants of the lower orders showed deficiency symptoms earlier than those of higher order.

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